THE

LONDON, EDINBURGH, AND DUBLIN

PHILOSOPHICAL MAGAZINE

AND

JOURNAL OF SCIENCE.

CONDUCTED BY

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"Nec aranearum sane textus ideo melior quia ex se fila gignunt, nec noster vilior quia ex alienis libamus ut apes." JUST. LIPS. *Polit.* lib. i. cap. 1. Not.

VOL. VII.—SEVENTH SERIES.

JANUARY—JUNE 1929.

LONDON:

TAYLOR AND FRANCIS, RED LION COURT, FLEET STREET.

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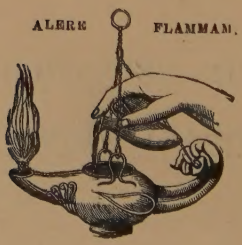
"Meditationis est perscrutari occulta; contemplationis est admirari perspicua .... Admiratio generat quæstionem, quæstio investigationem, investigatio inventionem."—*Hugo de S. Victore.*

——"Cur spirent venti, cur terra dehiscat,
Cur mare turgescat, pelago cur tantus amaror,
Cur caput obscura Phœbus ferrugine condat,
Quid toties diros cogat flagrare cometas,
Quid pariat nubes, veniant cur fulmina cœlo,
Quo micet igne Iris, superos quis conciat orbes
Tam vario motu."

J. B. Pinelli ad Mazonium.



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JOURNAL OF SCIENCE.

[SEVENTH SERIES.]

JANUARY 1929.

I. *Thermal Diffusion of Rare Constituents in Gas-mixtures.* By SYDNEY CHAPMAN, *F.R.S., Imperial College of Science and Technology, South Kensington, London* *.

I. *Thermal Diffusion and the Soret Phenomenon.*

§ 1. IT has been shown theoretically, by Enskog [1] and the writer [2] independently, that a gradient of temperature existing in a gas-mixture produces a motion of relative diffusion of the constituents, additional to and independent of any motion of diffusion that may be in progress, owing to a gradient of concentration or other cause. If the temperature gradient be maintained constant in a closed vessel, a steady state will result, in which there is a concentration gradient along the same direction, of amount just sufficient to effect a balance between the rates of diffusion due to the gradients. This phenomenon has been experimentally verified by Dootson [3], Ibbs [4], and Elliott & Masson [5].

§ 2. A similar phenomenon in liquids was discovered experimentally by Ludwig [6] and Soret [7] long before the theoretical discovery of thermal diffusion in gases ; it is generally known as the Soret phenomenon or Soret effect. Many attempts to provide a theory of it have been made [8], but none seems to have been successful. This is scarcely surprising if, as seems likely, the Soret phenomenon at its simplest is the analogue for liquids of thermal diffusion

* Communicated by the Author.

in gases, and may in many cases be further complicated by dissociation-effects depending on temperature, and, in electrolytes, by electric effects. There may be some hope of arriving at a simple theory in those cases, if any exist, where these additional causes are paramount; but where pure thermal diffusion is the only or main cause (and it will be shown in the following pages that thermal diffusion in gases is capable of producing concentration gradients of the same order of magnitude as are found in the Soret effect in many liquid solutions), the prospect of arriving at an even approximately correct theory seems rather remote. This is not only because of the additional difficulties present in every branch of the kinetic theory of liquids, as compared with the corresponding theory for gases, but because the theory of thermal diffusion even in gases is unusually complex.

§ 3. In the case of gases, no success has yet attended any attempts to develop a simple physical theory of thermal diffusion that will indicate even the sign of the phenomenon, *i. e.* that will show which constituent tends to flow towards the warmer region; the theory has been obtained only by a complete mathematical treatment of the equations of detailed transfer in the gas-mixture. Arguments, such as were used by Meyer, that lead to simple theories of viscosity and thermal conduction, are not effective in the case of thermal diffusion, as I have recently shown [9]; they are of too general a nature, and perhaps the reason why they are effective for viscosity and thermal conduction is because these phenomena likewise are general and unique in sign—friction always tending to retard relative motion, and heat to flow from hot regions to cold. But in thermal diffusion the constituent which tends towards the warmer region is generally, but not always, the lighter one, nor does the effect depend essentially on a difference of mass, since thermal diffusion can occur in mixtures of gases of equal molecular weight [10]. The effect depends both on the masses and on the diameters or fields of force of the molecules, in a manner expressible, even to a first approximation, only by formulæ of much complexity. The formulæ for the Soret effect in liquids and its dependence on the detailed physical properties of the molecules will probably be still more complicated.

§ 4. Though it is depressing thus to dwell on the difficulties which appear to beset the theoretical treatment of

the Soret phenomenon, a proper estimation of them may prevent waste of effort on unduly simple methods that are foredoomed to failure. It may be suggested that, where possible, any arguments on which it is proposed to base a theory of the Soret effect be first applied to the simpler case of thermal diffusion in gases, where an exact theory is available by which to test the results obtained. These remarks naturally do not apply to theories of the Soret effect in those cases, if any, where changes of dissociation, or electrical effects, can be shown to constitute the primary cause.

These considerations, applied to a recent attempt [11] by the writer to develop a theory of the Soret effect for Brownian grains suspended in a liquid at non-uniform temperature, led to the same unhopeful conclusion that the problem was too difficult for solution by the relatively elementary methods there used, though the work was not without valid and interesting results in relation to the distribution of the Brownian displacements in the case of non-uniform temperature.

II. *Thermal Diffusion of Rare Constituents in Gas-mixtures.*

§ 5. This work, however, turned my attention to the special case of thermal diffusion that bears most closely on the Soret effect as usually measured, namely, in solutions of small concentration. In this case the general formulæ for gas-mixtures become somewhat simplified, and it may be of interest to physicists and chemists to have them set out and illustrated by a few examples, particularly since the complete formulæ are repellent in their complexity.

The chief point of interest thus brought out is that thermal diffusion in gas-mixtures can produce a large proportionate change in the concentration of a rare constituent. Let the fractional concentration (by volume) of the two constituents be denoted by c_1, c_2, so that

$$c_1 + c_2 = 1. \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

Ordinary ratios of absolute temperatures (T) produce only small absolute changes in c_1 and c_2, whatever their values, and when neither c_1 nor c_2 is very small the change in either is a small proportion of the mean value, so that thermal diffusion seems to be a weak separating agent. But if c_1 (say) is very small, the difference between its values in the hot and cold regions of the containing vessel, though still small compared with unity, may be a large proportion

of the mean value of c_1. This fact may be of importance in some chemical or physical experiments where a rare constituent has special properties. Were it not for the continual mixing by winds, it would probably have an important influence on the distribution of the small amount of ozone which is known to exist in the upper atmosphere.

§ 6. The equation determining the steady distribution of a gas-mixture in which the absolute temperature T is variable in the direction of x (say) is

$$\frac{\partial c_1}{\partial x} = -k_T \frac{\partial T}{T \partial x}. \quad \ldots\ldots \quad (2)$$

No separate equation for c_2 is needed, since $c_2 = 1 - c_1$. The first constituent will be taken to be the rare one, so that c_1 will later be assumed small. In (2), $k_T = D_T/D_{12}$, where D_T and D_{12} are respectively the coefficients of thermal and ordinary diffusion[2]. It can be shown that k_T tends to zero with either c_1 or c_2, and that, writing

$$k_T = c_1 c_2 \alpha, \quad \ldots\ldots \quad (3)$$

in general α does not tend to zero with c_1 or c_2.

If c_1 is small, and c_2 therefore nearly equal to unity, (2) may be written in the approximate form

$$\frac{1}{c_1}\frac{\partial c_1}{\partial x} = -\frac{\alpha}{T}\frac{\partial T}{\partial x}. \qquad (c_1 \text{ small}). \quad (4)$$

In certain circumstances α may be treated as constant in this equation, and then there exists the simple solution

$$c_1 \propto T^{-\alpha}. \quad (c_1 \text{ small}, \alpha \text{ constant}) \quad (5)$$

In other cases α is approximately proportional to T^β, where β is a constant, and then (4) has the solution

$$\log_e c_1 = \text{constant} - \alpha/\beta, \quad (c_1 \text{ small}, \alpha \propto T^\beta). \quad (5\,a)$$

where now T is involved, on the right, through α.

The gas-mixture is here supposed to be at rest in a steady state in a tube or other vessel of which the dimensions are large compared with the molecular mean free paths, so that the pressure is uniform; α then depends only on c_1, T and the properties of the molecules. If the absolute change of c_1 along the tube is small, its influence on α will be negligible. The total variation of T along the tube is supposed not small, but in some cases α is independent of T, when (5) is the correct solution, while in other cases α is proportional to

T^{β} (where β is generally less than $\frac{1}{2}$), when $(5\,a)$ is the correct solution.

If α is positive, the proportion of the rare constituent will decrease towards the warmer regions; if negative, it will increase towards these regions. Either sign is possible, according to the nature of the molecules of both kinds.

III. *General Formulæ for the First Approximation to* α.

§ 7. The complete general expression for α is obtained in the form of the quotient of one infinite determinant by another, and only in one or two special cases can this expression be reduced to a simple form. In general it is impracticable to do more than consider the first few approximations to the complete expression, and even the first approximation, which alone will be considered here, is a lengthy formula. Fortunately it is correct to within a few units per cent.

The first approximation, which may be denoted by $\alpha(1)$, for the general case of spherically symmetrical molecules of any kind, is as follows, where M_1 and M_2 denote the molecular *weights* of the constituents 1 and 2 :

$$\alpha(1) = \frac{5}{2}\left\{\frac{1}{c_1\sqrt{M_2}}(\alpha_{01}\alpha_{1-1}-\alpha_{0-1}\alpha_{11})+\frac{1}{c_2\sqrt{M_1}}(\alpha_{0-1}\alpha_{1-1}-\alpha_{01}\alpha_{-1-1})\right\} \Big/ \left(a_{11}a_{-1-1}\alpha^2_{1-1}\right), \quad . \quad . \quad . \quad (6)$$

where

$$a_{11} = \alpha_{11} + (c_1/c_2)\alpha_{11}', \quad . \quad . \quad . \quad . \quad . \quad . \quad (7)$$

$$a_{-1-1} = \alpha_{-1-1} + (c_2/c_1)\alpha_{-1-1}, \quad . \quad . \quad . \quad . \quad . \quad (8)$$

and the various factors α_{rs} are independent of c_1 and c_2, but are complicated functions of the temperature and of the masses and other properties of the molecules. They can be expressed as follows :—

$$\alpha_{01} = \mu_2{}^2 M_1{}^{\frac{1}{2}}\left\{\Omega_{12}(1,2)-\frac{5}{2}\Omega_{12}(1,1)\right\}, \quad . \quad . \quad . \quad . \quad . \quad (9)$$

$$\alpha_{0-1} = -\mu_1{}^2 M_2{}^{\frac{1}{2}}\left\{\Omega_{12}(1,2)-\frac{5}{2}\Omega_{12}(1,1)\right\} = -\mu_{12}{}^{\frac{3}{2}}\alpha_{01}, \quad . \quad . \quad . \quad (10)$$

$$\alpha_{11}' = \frac{1}{3}\Omega_1(2,2), \qquad \alpha_{-1-1}' = \frac{1}{3}\Omega_2(2,2), \quad . \quad . \quad . \quad . \quad (11)$$

$$\alpha_{11} = \mu_2\left\{\left(\frac{55}{4}\mu_1^2 - \frac{25}{2}\mu_1 + \frac{25}{4}\right)\Omega_{12}(1,1) - 5\mu_2^2\Omega_{12}(1,2) + \mu_2^2\Omega_{12}(1,3) + \frac{4}{3}\mu_1\mu_2\Omega_{12}(2,2)\right\}, \quad . \quad . \quad . \quad (12)$$

$$\alpha_{1-1} = -(\mu_1\mu_2)^{\frac{3}{2}}\left\{\frac{55}{4}\Omega_{12}(1,1) - 5\Omega_{12}(1,2) + \Omega_{12}(1,3) - \frac{4}{3}\Omega_{12}(2,2)\right\}. \quad . \quad (13)$$

The expression for α_{-1-1} is obtainable from (12) by interchanging μ_1 and μ_2, which themselves are defined by

$$\left.\begin{aligned} \mu_1 &= \frac{M_1}{M_1+M_2}, \qquad \mu_2 = \frac{M_2}{M_1+M_2}, \\ \mu_{12} &= \mu_1/\mu_2 = M_1/M_2, \qquad \mu_{21} = 1/\mu_{12}, \end{aligned}\right\} \quad . \quad . \quad (14)$$

so that

$$\mu_1 + \mu_2 = 1. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (15)$$

In the above expressions $\Omega_{12}(l, n)$ denotes a certain function of T depending also on M_1, M_2, and the law of force between the unlike molecules; $\Omega_1(l, n)$ denotes the same function of the law of force between like molecules of the kind 1, M_2 in Ω_{12} being replaced in Ω_1 by M_1; similarly for Ω_2.

By virtue of the relations (7), (8), (10) the equation (6) can be written in the form

$$\alpha(1) = \tfrac{5}{2}\mu_{12}M_1^{-\frac{1}{2}}\alpha_{01}\frac{\begin{aligned} &c_1\{\mu_{12}\alpha_{11}' - \mu_{12}^{\frac{1}{2}}\alpha_{1-1} - \mu_{21}\alpha_{-1-1}\} \\ &- c_2\{\mu_{21}\alpha_{-1-1}' - \mu_{21}^{\frac{1}{2}}\alpha_{1-1} - \mu_{12}\alpha_{11}\} \end{aligned}}{\begin{aligned} &c_1^2\alpha_{11}'\alpha_{-1-1} + c_1c_2(\alpha_{11}\alpha_{-1-1} \\ &+ \alpha_{11}'\alpha_{-1-1}' - \alpha_{1-1}^2) + c_2^2\alpha_{11}\alpha_{-1-1}' \end{aligned}}, \quad . \quad . \quad . \quad (16)$$

where the dependence of α (1) upon c_1 and c_2 is completely explicit.

§ 8. In the following we shall consider specially the case where the molecules of the first kind are rare, so that c_1 tends to zero and c_2 to 1. In this case (16) becomes

$$\operatorname*{Limit}_{c_1 \to 0} \alpha(1) = \tfrac{5}{2}\mu_{12}M_1^{-\frac{1}{2}}c_{01}(\mu_{12}\alpha_{11} + \mu_{21}^{\frac{1}{2}}\alpha_{1-1} - \mu_{21}\alpha_{-1-1}')/\alpha_{11}\alpha_{-1-1}'. \quad . \quad (17)$$

Owing to the disappearance of α_{11}' from (17), this being the only term in (16) that depends on the law of force between the molecules 1 (*cf.* (11)), it is clear that the value of $\alpha(1)$, or the effect of thermal diffusion on the concentration gradient of the gas-mixture, does not depend on the nature of the interaction between the rare molecules. This is natural, since when c_1 tends to zero their mutual encounters are infinitely less frequent than their collisions with the molecules 2.

Two special forms of this limiting value of $\alpha(1)$ may be noted here, in which the rare molecules 1 are either infinitely heavier or infinitely lighter than the numerous molecules 2, *i. e.* the cases

$$(a) \quad \mu_1 \to 1, \quad \mu_2 \to 0;$$
$$(b) \quad \mu_1 \to 0, \quad \mu_2 \to 1.$$

It is evident, on inspection of (9), (11), (12), (13), that in case (*a*) only the first term in the numerator of (17) remains in the limiting expression (17), whereas in case (*b*) only the third term remains. Thus, on proceeding to the limits, we have

$$\underset{c_1 \to 0,\ \mu_2 \to 0}{\text{Limit}} \ \alpha(1) = \frac{15}{2} \frac{\Omega_{12}(1,2) - \frac{5}{2}\Omega_{12}(1,1)}{\Omega_2(2,2)}, \quad . \quad . \quad . \quad . \quad (18)$$

$$\underset{c_1 \to 0,\ \mu_1 \to 0}{\text{Limit}} \ \alpha(1) = -\frac{5}{2} \frac{\Omega_{12}(1,2) - \frac{5}{2}\Omega_{12}(1,1)}{\frac{25}{4}\Omega_{12}(1,1) - 5\Omega_{12}(1,2) + \Omega_{12}(1,3)}. \quad . \quad . \quad . \quad (19)$$

These results are independent of the order in which the two limits, for c_1 and μ_1, are approached.

§ 9. It may be noted that when the rare molecules are also the very light ones, the value of α is independent of the nature of the interaction between the numerous molecules 2 among themselves (*cf.* 19)). The latter move infinitely more slowly than the light molecules, owing to the approximate equality between the mean kinetic energies of peculiar motion of the molecules of the two kinds. Thus the heavy molecules are practically at rest, and the thermal diffusion depends only on the collisions of the rare, light, rapidly-moving molecules with the heavy stationary obstacles presented by the numerous molecules.

When, as in (18), the rare molecules are the heavy ones, thermal diffusion depends on the nature of the interaction both between the unlike molecules, and between the numerous light molecules among themselves.

It may also be remarked that case (*b*)—that of rare light molecules—is one of those in which the general theory of thermal diffusion can be replaced by a much simpler special theory, along lines first indicated by Lorentz [12] in connexion with the electron theory of metals. The exact expression for α (in place of the first approximation $\alpha(1)$ considered in (18)) can in this case be found. The general expression will not be given here, but in sections IV., V. the values for particular models will be quoted.

§ 10 The above formulæ can be further developed by inserting the appropriate values of the functions Ω. The general expressions for these functions will not be quoted here, but only the forms which they take for two specially simple types of molecular model, namely, rigid elastic spheres of diameters d_1, d_2, and point-centres of force varying as some constant (*s*th) power of the inverse mutual distance r, *i. e.* as r^{-s}; s will have suffixes 1, 12, or 2 according as the interaction refers to molecules 1 alone, 1 and 2, or 2 alone. The former model is, in a sense, a special case of the latter, corresponding to $s \rightarrow \infty$.

IV. *Rigid Elastic Spheres* *.

§ 11. In this case $\Omega(l, n)$ is independent of the first parameter l, being given, for all values of l, by

$$\Omega_{12}(l, n) = {}_1^1{}_6(n+1)\,!\,(d_1+d_2)^2\{2\mathrm{RT}(\mathrm{M}_1+\mathrm{M}_2)/\mathrm{M}_1\mathrm{M}_2\}^{\frac{1}{2}}, \quad . \quad . \quad . \quad (20')$$

where R denotes the gas-constant per gram-molecule, $8{\cdot}316 \,.\, 10^7$ ergs/°. Similarly

$$\Omega_2(l, n) = \tfrac{1}{2}(n+1)\,!\,d_2^2(\mathrm{RT}/\mathrm{M}_2)^{\frac{1}{2}}, \quad . \quad . \quad (21')$$

being obtained from (21′) by changing the suffix 1 to 2 throughout; likewise for $\Omega_1(l, n)$.

Consequently

$$\Omega(l, n) = (n+1)\Omega(l, n-1), \quad . \quad . \quad . \quad (22')$$

whence it follows that

$$\mathrm{M}_1^{-\frac{1}{2}}\alpha_{01} = \tfrac{1}{2}\mu_2^2\Omega_{12}(1, 1), \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (9')$$

$$\alpha_{11}' = \Omega_1(1, 1), \quad \alpha_{-1-1}' = \Omega_2(1, 1), \quad . \quad . \quad (11')$$

* The formulæ of this section are denoted by accented numbers (′) to indicate that they refer to a special model, and are not general, like those in the preceding sections: the formulæ of section V. are denoted by (″).

$$\alpha_{11}=\mu_2\left(\frac{13}{4}-\frac{5}{2}\mu_1+\frac{27}{4}\mu_1^2\right)\Omega_{11}(1,1), \quad . \quad (12')$$

$$\alpha_{1-1}=-\frac{27}{4}(\mu_1\mu_1)^{\frac{3}{2}}\Omega_{12}(1,1). \quad . \quad . \quad . \quad . \quad (13')$$

On substitution of these results into (17), this becomes

$$\underset{\epsilon_1\to 0}{\text{Limit}} \quad \alpha(1)=\frac{5}{4}\left\{(\tfrac{1}{2}\mu_1)^{\frac{1}{2}}(13-27\mu_1+44\mu_1^2)\left(\frac{d_1+d_2}{2d_2}\right)^2-4\mu_2\right\} \div(13-10\mu_1+27\mu_1^2). \quad (17')$$

On making μ_1 or μ_2 tend to zero, the following special cases of (18), (19) and the exact value of α in Lorentz's case are obtained:

$$\underset{c_1\to 0,\ \mu_2\to 0}{\text{Limit}} \quad \alpha(1)=\frac{5}{4\sqrt{2}}\left(\frac{d_1+d_2}{2d_2}\right)^2, \quad . \quad . \quad (18')$$

$$\underset{c_1\to 0,\ \mu_1\to 0}{\text{Limit}} \quad \alpha(1)=-\frac{5}{13}, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (19')$$

$$\underset{c_1\to 0,\ \mu_1\to 0}{\text{Limit}} \quad \alpha=-\frac{1}{2}. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (23')$$

V. *Molecules exerting Central Forces.*

§ 12. Suppose that the molecules are point-centres of force varying as r^{-s}, so that between unlike molecules 1, 2 the force is denoted by

$$K_{12}\frac{M_1M_2}{M_1+M_2}r^{-s_{12}}, \quad . \quad . \quad . \quad . \quad . \quad (24'')$$

and between two molecules 2, 2 by

$$\tfrac{1}{2}K_2M_2r^{-s_2}. \quad . \quad . \quad . \quad . \quad . \quad . \quad (25'')$$

The value of Ω in this case is given by

$$\Omega_{12}(l,n) = A(l,s_{12})\phi_{12}(s_{12})\Gamma\left(n+2-\frac{2}{s_{12}-1}\right), \quad (26'')$$

where

$$\phi_{12}(s_{12}) = \tfrac{1}{2}K_{12}^{\frac{2}{s_{12}-1}}\{2RT(M_1+M_2)/M_1M_2\}^{\frac{s_{12}-5}{s_{12}-1}}, \quad (27'')$$

and $A(l,s_{12})$ is a pure number obtained as an integral which can only be evaluated by quadrature. Its values for $l=1,2$ and various values of s are as follows, in terms of certain

integrals $I_1(s)$, $I_2(s)$ that have been evaluated by various writers [13] :—

$$A(1,s)=\frac{1}{2\pi}I_1(s), \qquad A(2,s)=\frac{3}{2\pi}I_2(s), \quad . \quad (28'')$$

$s=2$	3	5	7	9	11	15	21	25	∞
$I_1(s)=\ldots$	5·10	2·65	2·42	2·40	2·41	2·47	...	...	π
$I_2(s)=\ldots$	3·82	1·37	1·12	1·04	1·00	0·972	0·966	0·963	$\frac{1}{2}\pi$
$I_2(s)/I_1(s)=1$	1·33	1·93	2·16	2·31	2·41	2·54	...	...	3

By substituting the suffix 2 for 1 throughout in (26''), $\Omega_2(l,n)$ is obtained, and similarly for $\Omega_1(l,n)$.

In the present case

$$\Omega(l,n)=\left(n+1-\frac{2}{s-1}\right)\Omega(l,n-1), \quad . \quad (22'')$$

where Ω and s have the same suffix 1, 12, or 2. Consequently

$$M_1^{-\frac{1}{2}}\alpha_{01}=\mu_2^{\,2}\frac{s_{12}-5}{2(s_{12}-1)}\Omega_{12}(1,1), \quad . \quad . \quad (9'')$$

$$\alpha_{11}'=\frac{1}{3}\left(3-\frac{2}{s_1-1}\right)\Omega_1(2,1), \quad \alpha_{-1-1}'=\frac{1}{3}\left(3-\frac{2}{s_2-1}\right)\Omega_2(2,1), \quad . \quad . \quad . \quad (11'')$$

$$\alpha_{11}=\mu_2\left[\left\{\frac{55}{4}\mu_1^{\,2}-\frac{25}{2}\mu_1+\frac{25}{4}-5\mu_2^{\,2}\left(3-\frac{2}{s_{12}-1}\right)+\mu_2^{\,2}\left(3-\frac{2}{s_{12}-1}\right)\left(4-\frac{2}{s_{12}-1}\right)\right\}+\frac{4}{3}\mu_1\mu_2\left(3-\frac{2}{s_{12}-1}\right)\{A(2,s_{12})/A(1,s_{12})\}\right]\Omega_{12}(1,1), \quad . \quad . \quad . \quad (12'')$$

$$\alpha_{1-1}=-(\mu_1\mu_2)^{\frac{3}{2}}\left[\frac{55}{4}-5\left(3-\frac{2}{s_{12}-1}\right)+\left(3-\frac{2}{s_{12}-1}\right)\left(4-\frac{2}{s_{12}-1}\right)-\frac{4}{3}\left(3-\frac{2}{s_{12}-1}\right)\{A(2,s_{12})/A(1,s_{12})\}\right]\Omega_{12}(1,1). \quad (13'')$$

The corresponding form of (17) is too complicated to be worth quoting here, but the following are the special forms of (18), (19) and the exact form of α in Lorentz's case :—

$$\underset{c_1\to 0,\,\mu_2\to 0}{\text{Limit}} \quad \alpha(1)=\frac{15}{4}\frac{s_{12}-5}{s_{12}-1}\frac{s_2-1}{3s_2-5}\frac{A(1,s_{12})}{A(2,s_2)}\frac{\phi_{12}(s_{12})}{\phi_2(s_2)}, \quad (18'')$$

$$\lim_{c_1\to 0,\ \mu_1\to 0} \alpha(1) = -\frac{s_{12}-5}{s_{12}-1}\,\frac{5(s_{12}-1)^2}{13(s_{12}-1)^2-16(s_{12}-1)+16}, \quad . \ . \ . \quad (19'')$$

$$\lim_{c_1\to 0,\ \mu_1\to 0} \alpha = -\frac{s_{12}-5}{2(s_{12}-1)}. \quad . \ . \ . \ . \ . \ . \ . \ . \quad (23'')$$

It may be noted that when $s_{12}=5$, α is always zero, whatever the other circumstances. This is the case, specially considered by Maxwell, of molecules which repel one another according to the inverse fifth power of the distance; for such molecules thermal diffusion does not occur. The result is true whatever the interaction between the molecules 1 alone, or 2 alone.

For other values of s_{12}, the sign of thermal diffusion is different (*ceteris paribus*) according as s_{12} is greater or less than 5.

Owing to the last factor in (18''), $\alpha(1)$ in this case is not independent of T, as in the cases (18'), (19'), (23'), (19''), (23''): in (18'') it appears from (27'') that

$$\alpha(1) \propto T^{\beta}, \quad . \ . \ . \ . \ . \ . \ . \quad (29'')$$

where

$$\beta = \frac{1}{2}\left\{\frac{s_{12}-5}{s_{12}-1} - \frac{s_2-5}{s_2-1}\right\}; \quad . \ . \ . \quad (30'')$$

if, as for all ordinary gases, $s \geq 5$, β cannot exceed $\frac{1}{2}$.

§ 13. By comparison between (19'') and (23'') the ratio $\alpha(1)/\alpha$ for any value of s_{12} when $c_1\to 0$, $\mu_1\to 0$ can readily be found. The following table gives this ratio for various values of s_{12}, and also the ratio $\alpha(2)/\alpha$, where $\alpha(2)$ denotes the second approximation. These ratios refer exclusively to Lorentz's case, but give an idea of the degree of error involved in using $\alpha(1)$ in place of α; the error is greatest (for $s>5$) in the case $s=\infty$, corresponding to rigid elastic spherical molecules—*cf.* (19'), (23').

$s_{12}=$	2	3	5	9	13	17	∞
$\alpha(1)/\alpha=$	0·77	1·11	1·00	0·89	0·85	0·83	0·78
$\alpha(2)/\alpha=$	1·01	1·01	1·00	0·95	0·93	0·92	0·88

It appears from this table that for $s>5$ the approximations $\alpha(1)$, $\alpha(2)$ are less than α; the first approximation is good, and the second still better. When the molecular masses are nearly equal, the error of the first approximation appears to be less than in Lorentz's case.

§ 14. The expression (18)″ can be put into a much simpler form in terms of (i.) the coefficient of diffusion D_{12} of the mixture, at any pressure p and at the temperature T, and (ii.) the coefficient of viscosity ν_2 at temperature T, for the pure gas composed of the numerous, light constituent by itself—so long as we are content to use the first (fairly accurate) approximations $D_{12}(1)$, $\nu_2(1)$ to D_{12} and ν_2. For by (22)″

$$\underset{c_1\to 0,\,\mu_2\to 0}{\text{Limit}}\ \alpha(1)=\frac{15}{4}\frac{s_{12}-5}{s_{12}-1}\frac{\Omega_{12}(1,1)}{\Omega_2(2,2)}, \quad . \quad . \quad (31'')$$

while, quite generally,

$$D_{12}(1)=\frac{3}{16\pi^{\frac{1}{2}}}\frac{M_1+M_2}{M_1M_2}\frac{R^2T^2}{pN\Omega_{12}(1,1)}, \quad . \quad . \quad (32'')$$

$$\nu_2(1)=\frac{15}{16\pi^{\frac{1}{2}}}\frac{RT}{N\Omega_2(2,2)}, \quad . \quad . \quad . \quad . \quad . \quad (33'')$$

where N denotes the number of molecules per gram molecule. Consequently (when $M_2/M_1\to 0$),

$$\underset{c_1\to 0,\,\mu_2\to 0}{\text{Limit}}\ \alpha(1)=\frac{3}{4}\frac{s_{12}-5}{s_{12}-1}\frac{RT}{pM_2}\frac{\nu_2(1)}{D_{12}(1)}; \quad . \quad . \quad (34'')$$

this expression is independent of the value of p at which D_{12} is measured, since $D_{12}\propto 1/p$.

From (33″), (26″), and (27″) it appears that

$$\nu_2\propto T^{(s_2+3)/2(s_2-1)}, \quad . \quad . \quad . \quad . \quad . \quad (35'')$$

so that from a knowledge of the variation of ν_2 with temperature, s_2 can be inferred. For helium its value is approximately 14.

§ 15. It is of interest to examine how nearly the limiting formula (18′) for $\alpha(1)$ agrees with the true value of $\alpha(1)$ when M_1/M_2 is large (or μ_2 small) but not infinite; and likewise for (19′), when M_1/M_2 (or μ_1) is small but not zero. This can readily be done by inserting illustrative values of μ_1 and μ_2 in (17′) and comparing them with the values (18′) or (19′).

When μ_2 is small, d_2 is likely to be not greater than d_1, and extreme values of the ratio of $\alpha(1)$ to the limiting value of $\alpha(1)$ given by (18′) can be found by taking $d_2=0$ and $d_2=d_1$. In this way, when $\mu_2=\frac{1}{30}$, $\mu_1=\frac{29}{30}$, or $M_1/M_2=29$ the actual value of $\alpha(1)$ is less than that given by (18)′ by from 3·5 to 4·2 per cent.; when $\mu_2=\frac{1}{50}$, $\mu_1=\frac{49}{50}$, or

$M_1/M_2=49$, the corresponding limits of error are 2·1 and 2·5 per cent. Thus when M_1 is 50 or more times as great as M_2, (18′) affords a close approximation to the actual value of $\alpha(1)$; (18′) is larger than the true value of $\alpha(1)$, but the latter is less than the true value of α, so that (18′) is likely to be nearly correct.

The error of (19′) when μ_1 is small but not zero is rather larger than in the corresponding case for (18′). Here the limits of error are found by taking $d_1=0$ and $d_1=d_2$. If $\mu_1=\frac{1}{50}$, $\mu_2=\frac{49}{50}$, or $M_2/M_1=49$, the actual value of $\alpha(1)$ is less than that given by (19′) by from 8 to 12 per cent., though (19′) is likely to be nearly equal to the true value of α if M_2/M_1 has this value.

The corresponding percentage errors of the formulæ (18″), (19″), (34″), for values of s between ∞ and 5, are likely to be less than for (18′), (19′).

VI. *Numerical Illustrations and Suggestions for Experiment.*

§ 16. The order of magnitude of the concentration gradient produced by thermal diffusion in a closed vessel can be illustrated most readily from the simple formula (23″), corresponding to the case where the rare constituent is very light. In this case α, besides being known exactly, depends only on s_{12}. The following are values of $-\alpha$ for various values of s_{12} ; the case $s_{12}=\infty$ corresponds also to (23)′ :—

s_{12}:	∞	25	21	17	15	13	11	9	8	7	6	5
$-\alpha$:	·500	·417	·400	·375	·357	·333	·300	·250	·214	·167	·100	0

Since, by (5), $c_1 \propto T^{-\alpha}$, when α is constant, as here, the negative sign of α indicates that the proportion of the light rare constituent increases towards the hot region. The concentration-gradient produced may be illustrated by supposing the extreme absolute temperatures T, T′ (where $T'>T$) to be in the ratio $\frac{4}{3}$, as, for example, if $T=300°$, or 27° C., and $T'=400°$, or 127° C. The ratio of the corresponding values c_1, c_1' may be expressed as the percentage excess of c_1, *i. e.* by $100\left(\frac{c_1'}{c_1}-1\right)$, as in the following table :—

s_{12}:	∞	25	21	17	15	13	11	9	8	7	6	5
$100\left(\frac{c_1'}{c_1}-1\right)$ for $\frac{T'}{T}=\frac{4}{3}$:												
	15·4	12·7	12·2	11·4	10·9	10·1	9·0	7·5	6·4	4·9	2·9	0

§ 17. Much larger ratios of c_1 to c_1' for a given value of T'/T can be obtained, however, when the rare constituent is very heavy instead of very light. In this case (when $s>5$) the rare constituent, being heavy, is more concentrated in the cold than the hot region, since α is positive.

The maximum effect is obtained in the case of molecules which behave like rigid elastic spheres. If M_1 much exceeds M_2, d_1 is likely to exceed d_2. The following table gives the values of $\alpha(1)$ for a gas-mixture composed of rigid spherical molecules, for various likely values of the ratio d_1/d_2, from 1 to 3 ; $\alpha(1)$ is found from (18′) to vary from ·88 to 3·54, implying considerable percentage changes of concentration (here reckoned as the percentage excess of c_1 over c_1') even when T'/T is only $\frac{4}{3}$, as the table shows.

d_1/d_2:	1	$1\frac{1}{4}$	$1\frac{1}{2}$	$1\frac{3}{4}$	2	$2\frac{1}{4}$	$2\frac{1}{2}$	$2\frac{3}{4}$	3
$\alpha(1)$:	·884	1·12	1·38	1·66	1·99	2·32	2·97	3·10	3·54
$100\left(\frac{c_1}{c_1'}-1\right)$ for $\frac{T'}{T}=\frac{4}{3}$:	29	38	49	61	77	95	135	144	177

If $M_1/M_2>30$, these values of $\alpha(1)$ are unlikely to be less than the true values of α (*cf.* § 15), so that the large percentage changes of concentration are not over-estimated, for rigid spherical molecules.

§ 18. Most molecules, however, are "softer" than these, and correspond more nearly to molecules of the type considered in section V, for some finite value of s. The percentage excess of c_1 over c_1' for such molecules will be less than for the case $s=\infty$, and vanishes altogether for $s=5$. Moreover, unless $s_{12}=s_2$ so that $\beta=0$ (*cf.* (30″)), the law connecting the concentration c_1 with the temperature will not be $\log(c_1/c_1')=\alpha\log(T'/T)$, but that given by (5 *a*).

In this case, since $\alpha \propto T^\beta$,

$$\log_e\frac{c_1}{c_1'}=\frac{\alpha'-\alpha}{\beta}=\frac{\alpha}{\beta}\left\{\left(\frac{T'}{T}\right)^\beta-1\right\}. \quad . \quad . \quad (36'')$$

If the viscosity ν_2 of the light constituent (in the pure state) has been determined over a range of temperature, so that s_2 is known (*cf.* § 14), and if D_{12} is known at the temperature T and any pressure p, then α is a known multiple of $(s_{12}-5)/(s_{12}-1)$, and β is also known in terms of this quantity and s_2. Hence a measurement of c_1/c_1' suffices to determine s_{12}*, after which K_{12} can be determined from D_{12}.

* The actual solution is probably best made by calculating the right-hand side of (36″) for two or three values of s_{12}, and interpolating.

This seems to afford the simplest method of finding K_{12} and s_{12} when the heavy constituent is obtainable only in small quantities.

It may be noted that β will be positive or negative, according as s_{12} is $>$ or $< s_2$ (both being supposed not less than 5); the greatest value numerically is $\frac{1}{2}$, when one s is ∞ and the other 5, *i. e.* when in one set of inter-actions the numerous molecules behave like rigid spheres, and in the other like Maxwellian molecules, so that different forms of Ω must be used in the numerator and denominator of (18)—one from Section V., the other from Section VI.

In general $\{(T'/T)^\beta - 1\}/\beta$ differs little from $\log_e(T'/T)$ when T'/T is not too great: for example, if $T'/T = \frac{4}{3}$, $\log_e(T'/T)$ is ·218, while $\{(T'/T)^\beta - 1\}/\beta$ is ·268 if $\beta = -\frac{1}{2}$, and ·310 if $\beta = \frac{1}{2}$. In such cases a first approximation to α can be derived by using the simple formula $\log(c_1/c_1') = \alpha \log(T'/T)$, appropriate when α is constant; this will give a first approximation to s_{12}, and consequently to β, by (30″). Then a close second approximation to α can be made by using this value of β in (36″).

§ 19. Perhaps the most interesting and important application of these results is the determination of the law of force between helium molecules and those of radium emanation. The forces between molecules of the inert gases are of special interest because of their relation to the equilibrium of crystals in which the atoms are ionized—a subject studied by Born [14] and, very extensively, by Lennard-Jones [15]. Moreover, the radioactive property of the radium emanation enables its amount in a gas to be determinable with considerable accuracy, even when it is small. The mass-ratio of RaEm to He is 55·5, amply sufficient to justify the application of (18′) or (18″)—or (34″)—to a mixture in which the emanation is present to the extent of 2 or 3 per cent. at most. For helium v_2 and s_2 are known with ample accuracy, and in order to determine K_{12} and s_{12} it only requires a knowledge of D_{12} and $\log(c_1/c_1')$. The value of c_1/c_1' for $T'/T = \frac{4}{3}$ is not likely to be less than 1·2, corresponding to an excess concentration of RaEm by at least 20 per cent. in the cold region; the excess may well be much more, and can be increased by increasing the temperature ratio T'/T. Owing to the low concentration of the emanation, the time required for the steady concentration-gradient corresponding to the steady state of non-uniform temperature will be quite small.

It would also be of interest to determine in like manner the law of force between RaEm and the other inert gases Ne, A, Kr, Xe, though in these cases, since the mass-ratio is neither very large nor very small, the general formula (17) for α (1) must be used in working out the results, instead of the simpler special cases (18), (19). In all cases the RaEm may be a sufficiently rare constituent for (17) to be applicable, and no knowledge of the law of interaction between the RaEm molecules themselves is required. Another interesting gas-mixture, in which M_1/M_2 is large, so that (18) and its special forms (18′), (18″), (34″) can be used, is that of RaEm and hydrogen. Possibly other experiments might be made in which the heavy gas was mercury vapour, iodine vapour, or bromine vapour.

When accurate data of the kind suggested become available, it may be worth while to go to greater detail in the theory of thermal diffusion, considering further approximations to α, and taking account of the attractive force which most molecules appear to exert at greater distances.

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(8) Arrhenius, *K. Vet.-Ak. Förh.* ii. p. 61 (1894). Porter, Trans. Faraday Soc. xxiii. p. 314 (1927). Wereide, *Ann. Physique*, ii. p. 67 (1914), and many others.
(9) Chapman, Phil. Mag. v. p. 630 (1928).
(10) Chapman, Phil. Mag. xxxiv. p. 146 (1917).
(11) Chapman, Roy. Soc. Proc. A, cxix. pp. 34 & 55 (1928).
(12) Lorentz, 'Theory of Electrons,' Note 29; also Jeans, 'Dynamical Theory of Gases,' 4th edition, Ch. viii., §§ 288–295.
(13) Chapman, Mem. Manchester Lit. & Phil. Soc. lxvi. p. 1 (1922); also Lennard-Jones, Roy. Soc. Proc. A, cvi. p. 441 (1924).
(14) Born, 'Atomtheorie des festen Zustandes.'
(15) Lennard-Jones (and collaborators), Roy. Soc. Proc. A, cix. p. 584 (1925), cxii. p. 230 (1926), and numerous earlier papers there cited.

II. *On Groups of Electrons in the Geissler Discharge.* By K. G. Emeléus, *M.A., Ph.D., Lecturer in Physics, and* W. L. Brown, *M.Sc., Demonstrator in Physics, The Queen's University of Belfast* *.

1. *Introduction.*

In two previous communications †, accounts have been given of some results obtained by employing cold exploring electrodes to analyse glow discharges from cold cathodes, the methods used being those which have been developed by Langmuir and Mott-Smith ‡. The object of these investigations was to find the distribution of potential through a discharge which had no positive column, and to correlate the magnitudes of the electric fields in it with the concentrations and temperatures of the slow conducting electrons. In both, evidence was obtained that a group of fast electrons was present in the negative glow, including some with an energy of the order of 80 electron volts, but no detailed study of these was then made, since it was realized that more data would be required before even their existence could be regarded as definitely established. This uncertainty arises from the fact that fast electrons can only be detected when there is a sheath of positive ions round the collecting electrode, and that serious departures from the laws which should govern the reception of the latter have been recorded, although the discrepancies observed have now been at least partially removed §. The usual difficulties are, moreover, exaggerated in the present case by other unfavourable circumstances, the chief of which are :—

(*a*) The concentrations of ions and electrons are small, which makes it necessary to use relatively large collectors, upon which thick ionic sheaths form.

(*b*) Gas has to be used at a pressure of about 1 mm. Hg, so that the motion of a positive ion in traversing a thick sheath is not free, whilst the number of collisions that it makes is nevertheless not large.

(*c*) Conditions vary rapidly with position in the discharge, so that a collector is usually receiving ions and electrons

* Communicated by the Authors.

† Emeléus, Proc. Camb. Phil. Soc. xxiii. p. 531 (1927). Emeléus & Harris, Phil. Mag. iv. p. 49 (1927).

‡ Langmuir & Mott-Smith, Gen. El. Rev. 1924.

§ Penning, *Konink. Akad. Wet. Amsterdam,* xxxi. p. 1 (1927). Morse & Uyterhoeven, Phys. Rev. xxxi. p. 827 (1928).

from a region through which their concentrations are not constant.

For these reasons we have now made a more extended series of measurements, from which we have concluded that fast electrons, which will be referred to, initially without implication as to their origin, as *primary* electrons, are really present, and we have obtained, incidentally, some information about the slower *secondary* and *ultimate* groups which confirms and extends results already published.

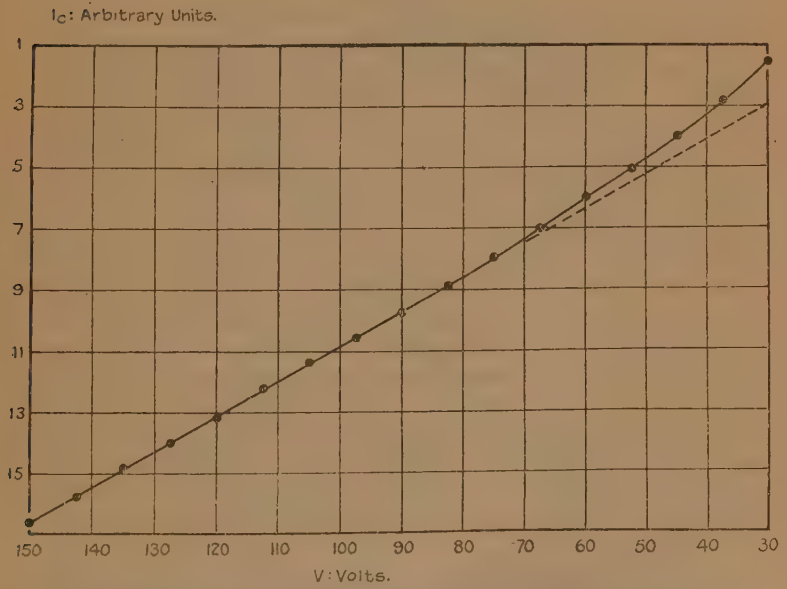
2. *Experimental Arrangements.*

The present arrangements have already been described *. Both thermionic diodes and wire resistances have been used to regulate the main discharge, currents of up to 5 milliamps. being passed at potentials between 250 volts and 400 volts. A switch was inserted so that the collector could be connected either to anode or cathode. In analysing the experimental data, we have worked with the ratio of the current to the collector to the current to the main cathode, to compensate approximately for fluctuations in the main discharge. The gases used were neon (containing 2 per cent. of helium), argon, hydrogen, and, for a few runs, oxygen. The argon was purified by arcing in the experimental tubes, or by passing a heavy glow discharge between magnesium electrodes in an auxiliary tube; hydrogen was admitted through a palladium regulator, whilst the oxygen was taken from a commercial cylinder. The discharge-tubes were cylinders, 3–4 cm. in diameter, and bulbs of various sizes. No attempt was made to obtain high purity of the gases, since it was felt that not enough was known of the general nature of the phenomena to warrant the elaborate precautions required to do this. The results were not affected, however, when mercury and carbon vapours were allowed access to the tubes by removal of liquid air from the traps. Glass-metal seals have been employed in most instances, and when this was impracticable, well-fitting dry joints made vacuum-tight with an external rim of picein. The collectors were usually bombarded with positive ions at 450 volts before taking a run, but omission to do this was again without effect. The pressure of the gas was recorded directly by a McLeod gauge, without any attempt being made to allow for local changes in temperature in the discharge-tube.

* Emeléus & Harris, Phil. Mag. iv. p. 49 (1927).

The first runs showed that the number of primary electrons was small, and that their distribution of velocities was approximately Maxwellian. Since the electron current to a collector at a given retarding potential is determined by its area, and the corresponding positive ion current by the outer area of the positive ion sheath, large collectors of small curvature were therefore used subsequently, with the object of keeping the ratio of the area of the sheath to the area of the collector as small and as nearly constant as possible.

Fig. 1.



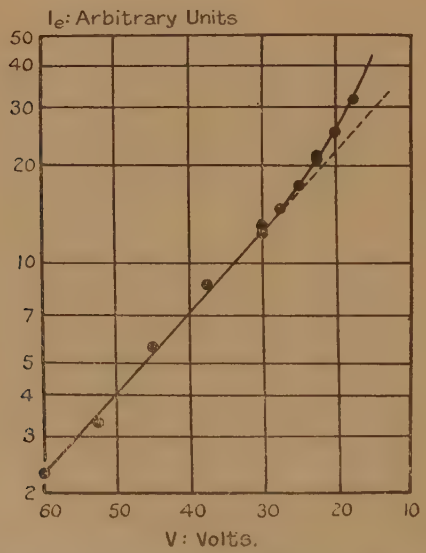
Net positive ion current to collector (I_c) for various potentials of collector negative to the anode (V): run 113.

3. *The Primary Group.*

Part of a collector characteristic, which is typical of some 150 which have been obtained in the present investigation from runs in the negative glow and Faraday dark space, is shown in fig. 1. The tube used was that described in § 4, the collector being in the middle of the negative glow, with its centre 0·25 cm. from the cathode, which was 0·90 cm. from the anode. The tube contained neon at a pressure of 1·37 mm. Hg, and was passing a current of 1·65 milliamps.

at 338 volts. For high accelerating potentials for positive ions the characteristic is practically linear, the current increasing with potential both because of the increase in the outer area of the sheath, and from causes referred to in § 1, but when about 70 volts negative to the anode, it takes a distinct additional upward trend. On extrapolating the almost straight part to lower collecting voltages, and analysing the difference between the experimental line and the extrapolated line by plotting current against voltage on semi-logarithmic paper in the usual way, three groups of

Fig. 2.



Semi-logarithmic plot of primary electron current (I_e) against collector potential negative to the anode (V).

electrons were found to be present. The line for the primary electrons is shown in fig. 2. The space potential was 10 volts negative to the anode. The difference between the two lines is at first small, and the primary temperature evidently cannot be found with great accuracy, so to obtain an idea of the reproducibility of the numbers, this run was made with the potential of the collector brought from a high negative potential through the space potential, and a second was then taken with the conditions otherwise unaltered, but the potential changes made in the reverse

direction. The temperatures recorded were 26·4, 3·9, 0·94 volts, and 26·4, 3·4, 0·96 volts respectively; the identity of the primary temperatures is fortuitous, and the error in their determination is not less than ± 3 volts. Two other examples of similar curves—in which all the experimental points are not shown—occur in fig 7.

Similar curves were obtained in the Faraday dark space in neon, argon, and hydrogen at various pressures, with a tube in which the cathode was a disk of nickel 0·85 cm. in diameter, backed with mica and supported by a glass-sheathed stem at the centre of a bulb 11 cm. in diameter; the anode was a piece of stout nickel wire situated close to the wall, and the collector a small cylinder of copper 1 mm. in diameter and 2 mm. long. The lead to the collector was separate from the pinch holding the leads for the anode and cathode. This showed that the appearance attributed to the primary group was not due to any action of the walls of the tube, nor to construction of the main discharge by the positive ion sheaths on the collector, which were often 3–4 mm. in diameter, and also made it improbable that it was due to collection from an inhomogeneous discharge, since conditions are more nearly uniform in the Faraday dark space than in the negative glow.

Runs in which the collector was a flat disk with a guard-ring gave characteristics of the same type, both when the guard-ring was held at the same potential as the disk and when it was floating, showing that the effect was not due to interaction between the positive ion sheaths on the collector and on neighbouring surfaces; the temperatures were the same in the two cases within the limits of experimental error. The primary group also appeared both when the collector was touching its insulating support in a part exposed to the discharge, and when it was protected from the discharge without actual contact.

The variety of conditions under which the primary group appears makes it very improbable that the effect is in any way due to the collector beginning to function as a main anode for the tube, especially since there is no marked change in the main current until the space-potential is passed and electrons begin to be collected in an accelerating field.

It was considered possible that the upward break in the characteristic might be due to a change in the type of motion of the positive ions, from an almost free fall through the thin sheaths present at small collecting voltages, to a species of mobility motion through the thicker sheaths present at higher collecting voltages. We have been unable to disprove

this by direct experiment, but we consider that the relatively sudden first appearance of the primary group is distinct from the likely changes in curvature of positive ion characteristics intermediate between some that we have computed on the one hand from Langmuir and Blodgett's tables for the free fall of ions *, and on the other from McCurdy's for collision motion †. The form of these computed curves does, however, show strongly the uncertainty of extrapolating to lower collecting voltages the positive ion line for higher collecting voltages.

During the course of this and the previous investigations, numerous tests were made to find if oscillations were occurring in the discharge system. Usually they were absent, but occasionally some of small amplitude, probably similar to those described by Appleton and West ‡, were detected. They were without effect upon the primary group. We have not examined the system by means of Lecher wires, but it is extremely unlikely that large amplitude oscillations of very high frequencies occurred with the small currents that were passed through our tubes §.

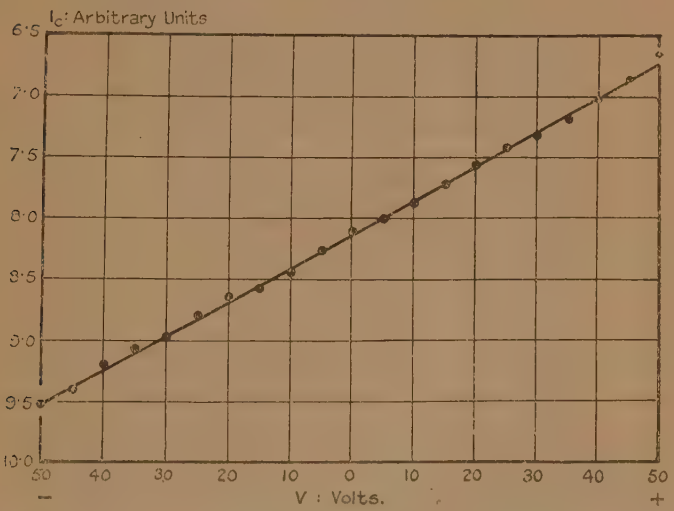
There is no systematic departure of the relation between log i and V for the primary group from the linear one required by a Maxwellian distribution of velocities, although some of the curves plotted on semi-logarithmic paper were definitely concave to the axis of voltage. However, no difference was found in this respect between the semi-log plots for a disk collector shielded from the cathode dark space and exposed to it, respectively, even although the collector was, from the appearance of the sheaths upon it, certainly drawing upon the ions in the cathode dark space in the latter case. The relation was likewise nearly linear for a collector consisting of a hemispherical piece of nickel, 2 mm. in diameter, placed with its axis perpendicular to the axis of the main discharge at the centre of curvature of a small hollow cathode, which would have been expected to concentrate any directed particles. It has nevertheless to be emphasized that large departures from a linear relation might pass unnoticed for the higher retarding voltages for electrons, because of the small differences between the experimental and the extrapolated lines, and also that a considerable drift velocity may be superposed upon a random

* Langmuir & Blodgett, Phys. Rev. xxii. p. 347 (1923).
† McCurdy, Phys. Rev. xxvii. p. 157 (1926).
‡ Appleton & West, Phil. Mag. xlv. p. 879 (1923).
§ *Cf.* Langmuir, Proc. Nat. Acad. Sci. xiv. p. 627 (1928).

motion without marked distortion of the linear semi-log plot*.

With some of the tubes used it has been possible to follow the positive ion line (*cf.* fig. 1) through the potential of the cathode without it showing any change. An example of this is shown in fig. 3. The collector was the hemispherical one previously mentioned, and was situated in the middle of the negative glow of a 295 volt discharge through hydrogen at a pressure of 0·59 mm. Hg ; the positive ion sheath preserved its normal appearance. In other cases the positive ion sheath developed bright inner and outer edges, whilst

Fig. 3.



Net positive ion current to collector (I_c) for various potentials of the collector relative to the cathode (V): run 26, collector acting normally.

the current to the collector increased more rapidly with increasing potential than at lower voltages. Fig. 4, which shows this, was obtained with neon in the bulb tube described earlier in this section, the gas-pressure being 2 03 mm. Hg and the tube voltage 238 ; the collector was in the Faraday dark space. The collector was then evidently acting as cathode for an auxiliary discharge, with the bright parts representing the cathode glow and the negative glow. If a small collector was used under these circumstances, it was liable to become

* Langmuir, Phys. Rev. xxvi. p. 585 (1925).

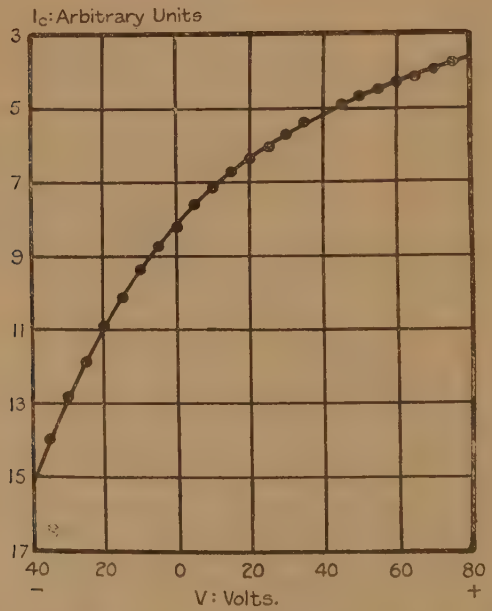
incandescent under the positive ion bombardment, particularly in argon, and an arc would strike to it.

It is concluded, from this evidence :—

(*a*) That the primary group of electrons is actually present in the discharge, and that the effects attributed to it are not inherent in the method of analysis.

(*b*) That the group has an approximately random distribution of velocities.

Fig. 4.



Net positive ion current to collector (I_c) for various potentials of collector relative to the cathode (V): run 63, collector acting as auxiliary cathode for main discharge.

(*c*) That it includes the majority of the fast electrons present, except very close to the cathode dark space (§ 4).

4. *Details of the Primary Group.*

The primary group was always present in the negative glow, where its average energy was usually between 20 and 45 electron-volts, irrespective of the gas used or of the applied potential. In the Faraday dark space it was absent

at the higher pressures, *e.g.* at a pressure of 1·5 mm. Hg in argon ; when present there, its energy was somewhat increased by an increase in the cathode fall in potential. Some results obtained with a tube 3 cm. in diameter, similar to that used in an earlier investigation, with both anode and cathode movable separately and fitting closely to the walls, are contained in Table I. The collector was an iron sphere, 0·32 cm. in diameter, situated on the axis of the tube. The fall of potential at the anode (run 107) is close to the ionization potential of neon (21·5 volts), as has been found by Penning *, when, as in this case, there was an anode glow present. The concentration of the primary group falls off on receding from the cathode far more rapidly than the concentrations of the slower groups.

TABLE I.

Run.	Collector to cathode, cm.	Space potential, volts negative to anode.	Temperatures, volts.			Concentrations, 10^7.			Position.
			I.	II.	III.	I.	II.	III.	
105 ...	0·48	21·5	19·2	4·0	0·5	3·7	38	332	Negative glow.
106 ...	0·62	20·0	34·5	3·9	1·2	2·5	36	142	Negative glow.
107 ...	0·90	20·0	32·2	11	1·9	0·3	22	121	Faraday dark space.

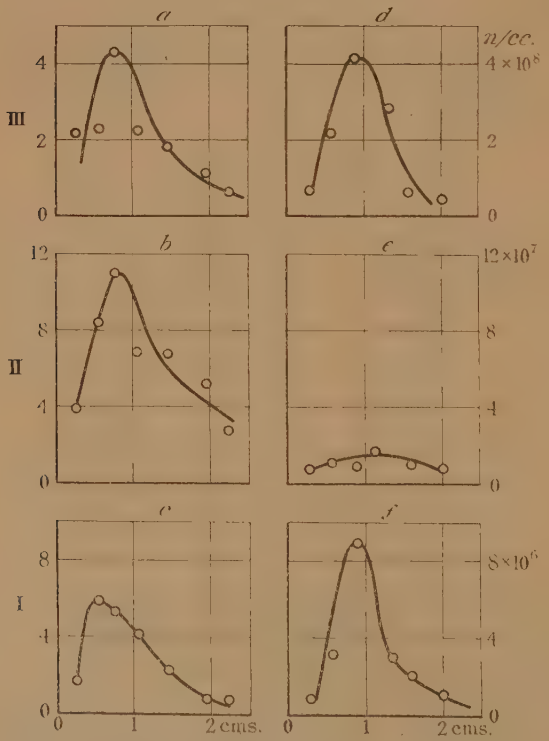
Tube described in § 4:—Gas-neon, pressure — 1·36 mm. Hg ; anode-cathode, 1·06 cm. ; current 3·3 milliamps. ; applied potential, 385 volts ; anode glow present.

Other results obtained with the same system of electrodes are collected in fig. 5, *a–f*, and fig. 6, *g–l*. Both refer to discharges through argon, the pressures being 1·10 mm. Hg (*a–c*, *g–i*) and 0·41 mm. Hg (*d–f*, *j–l*), the applied potentials 370 and 374 volts, and the tube currents 0·75 milliamp. and 0 79 milliamp. respectively. In the former case the cathode dark space was about 0·35 cm. thick, and in the latter about 0·5 cm. The main electrodes were 2·85 cm. apart in each case, and there was no anode glow. In the figures the numerals I., II., and III. refer to the primary, secondary, and ultimate electrons respectively, and the distances are measured from the cathode ; the centre of the negative glow occurred at about the maximum of concentration for the ultimate electrons. The gas was sufficiently pure to show a primary

* Penning, *Physica*, v. p. 217 (1925).

dark space *. At the higher pressure there was a direct anode fall in potential of 7 volts, and at the lower pressure a reversed anode fall in potential of 10 volts. Local changes are, of course, inevitably smoothed over by the use of a large collector, but bearing this in mind, the curves for the secondary and ultimate groups are concordant with those obtained by Emeléus and Harris. In particular, the ultimate

Fig. 5.



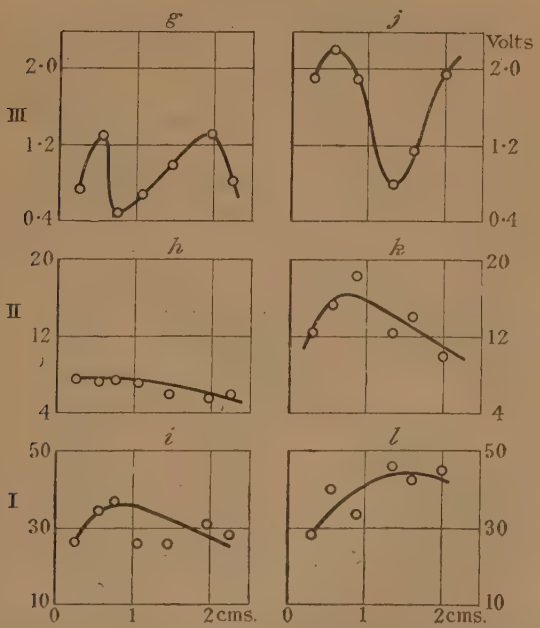
Concentration curves for groups of electrons: runs 127–133 (*a–c*) and 143–148 (*d–f*).

electrons carry most of the random current, and the secondary electrons, which were not detected at the lower pressure before, are here only present in small numbers at 0·41 mm. Hg. In corresponding parts of the discharge the electron temperatures are higher at the lower pressures.

* Aston & Watson, Proc. Roy. Soc. A, lxxxvi. p. 168 (1912).

The points on the curves of concentration and temperature for the primary electrons (*c*, *f*, *i*, *l*), in drawing which account has been taken of the results of other series of runs, although somewhat scattered, exhibit certain regular features. The temperatures are again higher at the lower pressure, and, as has also been found in numerous other runs, both temperatures and concentrations have a maximum at about the brightest part of the negative glow at the higher pressure, and the concentration, if not also the temperature,

Fig. 6.



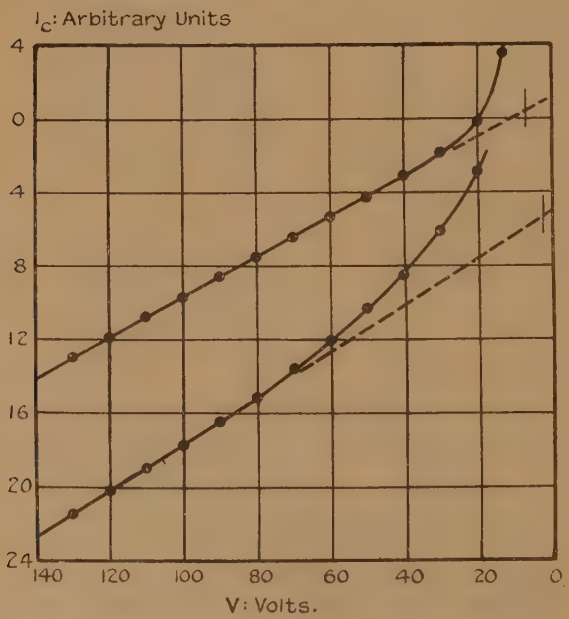
Temperature curves for groups of electrons: runs 127–133 (*g–i*) and 143–148 (*j–l*).

a maximum there at the lower pressure. These observations are intimately connected with another point noticed in the present work, and in that of Emeléus and Harris*, which is illustrated by fig. 7, in which parts of a pair of collector characteristics used in connexion with figs. 5 and 6 are reproduced. The space potentials are shown by vertical lines on the produced positive ion lines. To the negative side

* Emeléus & Harris, Phil. Mag. iv. p. 49 (1927).

of the negative glow—upper curve—the latter extrapolates to an electron current at the space-potential; in parts of the discharge more remote from the cathode—lower curve—the line extrapolates to a positive ion current at the space-potential. The uncertainty involved in the extrapolation is probably such that the positive ion line should actually cross the voltage axis on the negative side of the space-potential more frequently than we have assumed. Near to the cathode there are apparently faster electrons than those

Fig. 7.



Net positive currents to collector (I_c) for various potentials of the collector negative to the anode (V) under different conditions: runs 133 (above) and 132 (below).

in the primary group included with the positive ions, although it has hitherto been impossible to resolve them. The only work we have been able to trace in which it has been shown directly that fast electrons occur in the cathode dark space or negative glow for a cathode fall in potential of a few hundred volts is that of Dauvillier *, who detected photo-electrically the L-radiation of argon, which requires for its

* Dauvillier, *Journ. d. Physique*, vii. p. 369 (1926).

excitation not less than 240 volts, from near the positive boundary of the cathode dark space under similar conditions. The evidence usually adduced in support of their presence from spectro-photometric studies of the negative glow does not take sufficient account of the complicated process that may give rise to the emission of light there.

5. *Discussion of Results.*

The data obtained so far are inadequate to serve as a basis for a complete test of the theory of the negative glow and Faraday dark space given by Morse*, and are being extended, but certain points may be considered at this stage. It appears probable from the results of § 4 that the primary group is initially formed in the negative side of the negative glow from a faster and probably directed stream of electrons entering it from the cathode dark space, and that the existence of a maximum of ionization and luminosity in the middle of the negative glow is connected with the full development of the primary group. The average energy of the primary electrons in this part of the discharge is also about what would be expected on this view of their origin from Langmuir and Jones's measurements of the mean free paths of electrons †, taken in conjunction with K. T. Compton and Morse's theoretical analysis of the normal cathode dark space ‡. The approximately Maxwellian distribution of velocities found in the primary group is understandable in view of the small electric field in the negative glow, and the still unexplained fact that groups of electrons acquire a random motion in a region of intense ionization more readily than can be explained on the usual kinetic grounds §.

The persistence of the primary group in the Faraday dark space is less readily accounted for, since it has long been recognized that even faster electrons than those now under consideration cannot penetrate far into it. Their distribution of velocities indicates however, that they are in some sort of equilibrium, in which those which disappear by collision and by diffusion to the walls are partly regenerated by another agent, whilst the value of their average energy, which is usually somewhat above that required for ionization of the gas-molecules, suggests that some effect of the neutralization of positive ions may come into play. A

* Morse, Phys. Rev. xxxi. p. 1003 (1928).
† Langmuir & Jones, Phys. Rev. xxxi. p. 357 (1928).
‡ K. T. Compton & Morse, Phys. Rev. xxx. p. 305 (1927).
§ Langmuir, *Zeits f. Physik*, xlvi. p. 271 (1928).

mechanism which might produce new primary electrons is the converse of ionization by collision, with a system of two slow electrons and one positive ion passing into one consisting of a neutral, probably excited molecule, and a single fast electron. Lines of O III. and Ne III. occur in the spectrum of the negative glow of a discharge at 440 volts *, so that the recombination would include the partial neutralization of multiply-charged ions, with production of faster electrons than in the neutralization of singly-charged ions. Paschen has found continuous spectra beyond the series limits in the spectrum of the light from the negative glow in helium †, showing that the corresponding two-body interaction of a single slow electron and a positive ion, which results in the production of a neutral atom and radiation takes place, although it is not clear how this observation can be reconciled with the three-body theory of the recombination of ions proposed by J. J. Thomson ‡. Primary electrons might be formed in a positive column in this way, but although some curves which we have obtained in neon could be taken to indicate that they are present, further investigation of this part of the discharge is desirable. If this explanation of the persistence of the primary group in the Faraday dark space is correct, it would be expected to have a less energy, probably of the order of 12 volts, in discharges through mercury vapour, with an ionization potential of 10·4 volts.

It is very puzzling why two groups of slow electrons should be present in this and other discharges, although there is now no question of their separate existence §. There is no evidence as to how far these secondary and ultimate groups are produced directly from the primary group by collisions with gas-molecules, and how far they are produced by processes involving cumulative ionization and ionization by metastable atoms and by radiation. In gases in which there is a Ramsauer minimum of the free paths of electrons, this will tend to maintain the slow electrons in two groups, of greater and less energy than corresponds to the minimum, which does, in fact, often occur at about the average energy of the secondary and ultimate groups.

6. *Summary.*

Measurements of collector characteristics have been made in the Geissler discharge from a cold cathode in argon, neon,

* F. M. Chambers & N. M. Carmichael (unpublished work).
† Paschen, *Sitz. Preuss. Akad. Wiss.* xvi. p. 135 (1926).
‡ J. J. Thomson, Phil. Mag. xlvii. p. 337 (1924).
§ v. Voorhis, Phys. Rev. xxx. p. 318 (1927).

hydrogen, and oxygen, at pressures of about 0·1 cm. Hg, for conditions not far from those at normal cathode fall of potential, from which it is concluded that there is present in the negative glow, and at the low pressures, in the Faraday dark space, a group of fast electrons with a distribution of velocities that is approximately Maxwellian, and an average energy of the order of 25 electron-volts. It is suggested that they are produced initially by electrons passing into the negative glow from the cathode dark space, and that they are maintained by a process which is the reverse of ionization by collision. A possible effect of the Ramsauer minimum of the free paths of electrons is pointed out, in the persistence of two groups of slow electrons in the discharge.

We are indebted to Prof. E. V. Appleton, F.R.S., for a gift of copper-clad wire and valve pinches which has materially reduced the labour of building the numerous tubes required.

III. *Three-Dimensional Motion of an Electron in the Field of a Non-Neutral Atom.* *By* M. A. Higab, *M.Sc., Ph.D., Lecturer in Applied Mathematics in the Egyptian University, Cairo* *.

IN the Phil. Mag. xx. pp. 244–245 (1910) an attempt to deal with the three-dimensional motion of a particle under the effect of a doublet was made by Sir J. J. Thomson. In this paper, although the equations of motion were integrable, yet Sir J. J. Thomson considered only steady motion. The problem was resumed by Sir J. H. Jeans in the Phil. Mag. xx. pp. 380–382 (1910), who integrated the equations of motion and obtained certain results of interest. Physicists are generally convinced that the structure of a neutral atom of an element follows the lines associated with the names of Rutherford and Bohr. In such an atom the total charge is zero, and it behaves towards an electron sufficiently far away like a doublet.

Suppose that by some means or other this neutral atom loses or gains a charge. In this case the atom behaves like an electric doublet plus or minus an electric charge.

The problem is thus "To find the motion of an electron

* Communicated by Prof. A. M. Mosharrafa.

(supposed to be negatively charged) under the effect of an electric doublet, acted upon at the same time by a central force inversely proportional to the square of the distance from the doublet itself."

We shall assume that the electron carries unit charge per unit mass, and that the electric charge is placed at the centre of the doublet ; also that the axis of the doublet is fixed.

The problem is, as a matter of fact, suggested by Sir G. Greenhill (Phil. Mag. xlvi. pp. 372, 376, 1923), who, however, restricts the discussion to two dimensions. He shows that the problem can be dealt with in connexion with Euler's method for the path of a particle in the field of two fixed spheres. Sir G. Greenhill suggests the discussion of possible closed figures, and it is the object of the present paper to investigate the possibility of formations of closed orbits in the three-dimensional case.

The equations of motion are as follows. Let $r=\mathrm{OP}$ be the distance of the electron from O, the centre of the doublet, and θ the angle which OP makes with the axis of the doublet, and ϕ the angle which the plane POB makes with a fixed plane.

The equations of motion are

$$\ddot{r}-r\dot{\theta}^2-r\sin^2\theta\dot{\phi}^2=-\frac{\mu}{r^2}-\frac{2\lambda\cos\theta}{r^3}, \quad . \; . \; (1)$$

$$\frac{1}{r}\frac{d}{dt}(r^2\dot{\theta})-r\sin\theta\cos\theta\dot{\phi}^2=-\frac{\lambda\sin\theta}{r^3}, \quad . \; . \; (2)$$

$$r^2\sin^2\theta\dot{\phi}=h, \quad . \; . \; . \; . \; . \; . \; (3)$$

where λ is the strength of the doublet and is positive, μ is the constant of the central force and is either positive or negative, and h is constant.

There are three types of motion, which are to be considered separately :—

I. Motion on a right circular cone defined by $\theta=$constant.

II. Motion on a sphere defined by $r=$constant.

III. General motion, where all the coordinates vary.

I. Motion on a Right Circular Cone.

Putting $\theta=\alpha$ (where α is constant) in the equations (1), (2), (3), we get the equations of motion to be

$$\ddot{r} - r\sin^2\alpha\dot{\phi}^2 = -\frac{\mu}{r^2} - \frac{2\lambda\cos\alpha}{r^3}, \quad \ldots \quad (1)$$

$$r^4\dot{\phi}^2 = \lambda\sec\alpha, \quad \ldots \quad (2)$$

$$r^4\dot{\phi}^2 = h^2\operatorname{cosec}^4\alpha. \quad \ldots \quad (3)$$

The equations (2) and (3) are identical if

$$h^2 = \lambda\tan\alpha\sin^3\alpha.$$

Since h^2 is positive, we must have $0 < \alpha < \frac{\pi}{2}$. If $\alpha = 0$, then $h = 0$, *i. e.* the motion is along the line $\alpha = 0$; if $\alpha = \frac{\pi}{2}$, then the force perpendicular to r in the plane containing r and the axis of the doublet must vanish, i. e. r must be infinite, for λ is not equal to zero. In this case the motion is at infinity.

Circular Motion.

If $r = a$, where a is constant, the electron moves on a circle in a plane perpendicular to the axis of the doublet. In this case we have

$$\cos\alpha = -\frac{\mu a}{6\lambda} + \sqrt{\frac{\mu^2 a^2}{36\lambda^2} + \frac{1}{3}},$$

$$\omega^2 = \frac{\lambda}{a^4}\sec\alpha,$$

$$h = \pm a\sin^2\alpha\,\omega.$$

This is exactly the same case as that discussed on p. 42.

General Motion.

Eliminating $\dot{\phi}$ between (1) and (2), we get

$$\ddot{r} = -\frac{\mu}{r^2} + \frac{A}{r^3}, \quad \ldots \quad (4)$$

where $$A = \frac{\lambda(3\sin^2\alpha - 2)}{\cos\alpha}.$$

The first integral of (4) is

$$\dot{r}^2 = \frac{2\mu}{r} - \frac{A}{r^2} + B, \quad \ldots \quad (5)$$

where B is constant.

Thus the differential of the path is

$$\frac{1}{r^4}\left(\frac{dr}{d\phi}\right)^2=\frac{\cos\alpha}{\lambda}\left[\frac{2\mu}{r}-\frac{A}{r^2}+B\right].$$

Putting $u=\frac{1}{r}$, and writing $\frac{du}{d\theta}=w_1$, we get

$$u_1^2=\frac{\cos\alpha}{\lambda}[2\mu u-Au^2+B]. \quad . \quad . \quad . \quad . \quad (6)$$

The following cases are to be discussed separately —

(*a*) A positive.

(*b*) A zero.

(*c*) A negative.

Case (*a*).—A positive, *i. e.* $\sin\alpha>\sqrt{\frac{2}{3}}$.

(i.) μ positive.

The differential equation of the path is

$$u_1^2=\frac{A\cos\alpha}{\lambda}\left[\frac{B}{A}+\frac{\mu^2}{A^2}-\left(u-\frac{\mu}{A}\right)^2\right]$$

$$=\frac{A\cos\alpha}{\lambda}\left[\frac{e^2}{l^2}-\left(u-\frac{1}{l}\right)^2\right],$$

where $\frac{B}{A}+\frac{\mu^2}{A^2}=\frac{e^2}{l^2}$ and $\frac{\mu}{A}=\frac{1}{l}$.

Now $u_1=0$ at $u=\frac{1\pm e}{l}$.

If $e<1$, then r oscillates between the maximum and minimum values $\frac{l}{1-e}$ and $\frac{l}{1+e}$ respectively. In this case it is possible for periodic orbits to be formed.

If $e\geq 1$, then the maximum value of r is infinite. No periodic orbits exist in this case. Thus the path is always open.

The equation of the path is

$$\frac{l}{r}=1+e\cos\left[\left(\frac{A\cos\alpha}{\lambda}\right)^{\frac{1}{2}}\phi+C\right], \quad . \quad . \quad . \quad (7)$$

where C is constant.

Periodic Orbits.

Let the initial conditions be $r=r_0$, $\phi=\phi_0$. The equation (7) becomes

$$\frac{l}{r}=1+e\cos\left[\cos^{-1}\left(\frac{l}{r_0}-1\right)\Big/e-\left(\frac{A\cos\alpha}{\lambda}\right)^{\frac{1}{2}}\phi_0+\left(\frac{A\cos\alpha}{\lambda}\right)^{\frac{1}{2}}\phi\right].$$

For periodic orbits to be formed, we must have, in addition to $e<1$,

$$\left(\frac{A\cos\alpha}{\lambda}\right)^{\frac{1}{2}}2k\pi=2m\pi,$$

$$i.\,e. \qquad \frac{A\cos\alpha}{\lambda}k^2=m^2,$$

where k and m are positive integers.

This condition gives

$$\sin\alpha=\sqrt{\frac{m^2}{3k^2}+\frac{2}{3}}.$$

The periodic orbits of the first order are given by $k=1$. It is obvious that they do not exist.

The periodic orbits of the second order are given by $k=2$. There is only one periodic order of that type, and that is given by $m=1$.

The periodic orbits of the third order are given by $k=3$. There are only two periodic orbits of that type, and these are given by $m=1$ and 2 respectively.

Similarly for orbits of higher order.

Thus we have established the existence of an infinite number of periodic orbits on the surface of a right circular cone.

(ii.) μ negative.

Put $\mu=\mu'$, where μ' is positive.

The differential equation of the path is

$$u_1^2=\frac{A\cos\alpha}{\lambda}\left[\frac{e^2}{l^2}-\left(u+\frac{1}{l}\right)^2\right],$$

where $\dfrac{B}{A}+\dfrac{\mu'^2}{A^2}=\dfrac{e^2}{l^2}$ and $\dfrac{\mu'}{A}=\dfrac{1}{l}$.

If $e<1$, no motion is possible.

If $e=1$, the motion is altogether at infinity.

If $e>1$, r passes through the minimum value $\dfrac{l}{e-1}$ and then proceeds to infinity.

Thus no periodic orbits exist in this case.

The equation of the path is

$$\frac{l}{r} = -1 + e\cos\left[\left(\frac{A\cos\alpha}{\lambda}\right)^{\frac{1}{2}}\phi + C\right],$$

where C is constant.

Case (*b*).—A=0, *i.e.* $\sin\alpha = \sqrt{\frac{2}{3}}$.

(i.) μ positive.

The differential equation of the path is

$$u_1^2 = \frac{\cos\alpha}{\lambda}[2\mu u + B].$$

If B is positive, the electron goes to infinity if projected away from the origin, arriving there with a velocity $\sqrt{B}$; but goes to the origin if projected towards it, arriving there with infinite velocity. Thus the path is always open.

The equation of the path is

$$\frac{1}{r} = \frac{1}{4}\left[\left(\frac{2\mu\cos\alpha}{\alpha}\right)^{\frac{1}{2}}\phi + C\right]^2 - \frac{B}{2\mu}.$$

If B is negative, then the maximum value of r is $\frac{2\mu'}{B'}$, where $B' = -B$. Thus the electron goes to the origin if projected away from or towards the origin.

The equation of the path is

$$\frac{1}{r} = \frac{1}{4}\left[\left(\frac{2\mu\cos\alpha}{\lambda}\right)^{\frac{1}{2}}\phi + C\right]^2 + \frac{B'}{2\mu}.$$

(ii.) μ negative.

Put $\mu = -\mu'$, where μ' is positive.

The differential equation of the path is

$$u_1^2 = \frac{\cos\alpha}{\lambda}[B - 2\mu' u].$$

Here B must be positive. The minimum value of r is given by $\frac{\mu'}{B}$, after which the electron goes to infinity.

The equation of the path is

$$\frac{1}{r}\frac{B}{2\mu} - \frac{1}{4}\left[\left(\frac{2\mu\cos\alpha}{\lambda}\right)^{\frac{1}{2}}\phi + C\right]^2.$$

CASE (*c*).—A negative, *i. e.* $\sin\alpha < \sqrt{\frac{2}{3}}$.

(i.) μ positive.

The differential equation of the path is

$$u_1^2 = \frac{A\cos\alpha}{\lambda}[2\mu u - Au^2 + B].$$

Put $A = -A'$, where A' is positive; then we get

$$u_1^2 = \frac{A'\cos\alpha}{\lambda}\left[\frac{B}{A'} - \frac{\mu^2}{A'^2} + \left(u + \frac{\mu}{A'}\right)^2\right].$$

Now, if $\frac{B}{A'} - \frac{\mu^2}{A'^2}$ is positive, we can put

$$\frac{B}{A'} - \frac{\mu^2}{A'^2} = \frac{e^2}{l^2} \quad \text{and} \quad \frac{\mu'}{A} = \frac{1}{l}.$$

The differential equation of the path becomes

$$u_1^2 = \frac{A'\cos\alpha}{\lambda}\left[\frac{e^2}{l^2} + \left(u + \frac{1}{l}\right)^2\right].$$

In this case the radial velocity of the electron does not vanish and r does not oscillate. Thus no periodic orbits exist. If the electron is projected away from the origin it goes to infinity, but if projected towards the origin it arrives there.

The equation of the path is

$$\frac{l}{r} = -1 + e\sinh\left[\left(\frac{A'\cos\alpha}{\lambda}\right)^{\frac{1}{2}}\phi + C\right],$$

where C is constant.

If $B = \frac{\mu}{A'}$ the electron goes to the origin if projected toward it, but goes to infinity if projected away from the origin. Thus the path is always open and no periodic orbits exist.

The equation of the path is

$$\log\left[\frac{1}{r} + \frac{1}{l}\right] = C + \left(\frac{A'\cos\alpha}{\lambda}\right)^{\frac{1}{2}}\phi,$$

where C is constant.

If $\frac{B}{A'} - \frac{\mu^2}{A'^2}$ is negative, then the differential equation of the path can be put in the form

$$u_1^2 = \frac{A' \cos \alpha}{\lambda} \left[\left(u + \frac{1}{l} \right)^2 - \frac{e^2}{l^2} \right],$$

where $$\frac{B}{A'} - \frac{\mu^2}{A'^2} = -\frac{e^2}{l^2} \quad \text{and} \quad \frac{\mu}{A'} = \frac{1}{l}.$$

The equation of the path is

$$\frac{l}{r} = -1 + e \cosh \left[C + \left(\frac{A' \cos \alpha}{\lambda} \right)^{\frac{1}{2}} \phi \right],$$

where C is constant.

If $e > 1$ the maximum value of r is $\frac{l}{e-1}$, in which case the electron falls towards the doublet.

If $e \leqslant 1$ the electron goes to infinity if projected away from the origin, but goes to the origin if projected toward it.

(ii.) μ negative.

Put $A = -A'$, where A' is positive,

and $\mu = -\mu'$, where μ' is positive.

The differential equation of the path is

$$u_1^2 = \frac{A' \cos \alpha}{\lambda} \left[\frac{B}{A'} - \frac{\mu'^2}{A'^2} + \left(u - \frac{\mu'}{A'} \right)^2 \right].$$

If $\frac{B}{A'} - \frac{\mu'^2}{A'^2}$ is positive, the differential equation of the path can be put in the form

$$u_1^2 = \frac{A' \cos \alpha}{\lambda} \left[\frac{e^2}{l^2} + \left(u - \frac{1}{l} \right)^2 \right],$$

where $$\frac{B}{A'} - \frac{\mu'^2}{A'^2} = \frac{e^2}{l^2}$$

and $$\frac{\mu'}{A'} = \frac{1}{l}.$$

The equation of the path is

$$\frac{l}{r} = 1 + e \sinh \left[C + \left(\frac{A' \cos \alpha}{\lambda} \right)^2 \phi \right]$$

where C is constant.

This path is always open. The electron goes to infinity if projected away from the origin, but goes to the origin if projected towards it.

If $B=\frac{\mu'^2}{A'}$, the differential equation of the path is

$$u_1^2=\frac{A'\cos\alpha}{\lambda}\left(u-\frac{1}{l}\right)^2.$$

Thus the equation of the path is

$$\log\left(\frac{1}{r}-\frac{1}{l}\right)=C+\left(\frac{A'\cos\alpha}{\lambda}\right)^{\frac{1}{2}}\phi,$$

where C is constant.

This path is always open. No periodic orbits exist.

If

$$\frac{B}{A'}-\frac{\mu'^2}{A'^2}=-\frac{e^2}{l^2} \quad \text{and} \quad \frac{\mu'}{A'}=\frac{1}{l},$$

then the differential equation of the path is

$$u_1^2=\frac{A'\cos\alpha}{\lambda}\left[\left(u-\frac{1}{l}\right)^2-\frac{e^2}{l^2}\right].$$

In this case r has either the minimum value $\frac{l}{1-e}$ or the maximum value $\frac{l}{1+e}$, *i.e.* the motion is either outside $r=\frac{l}{1-e}$ and extends to infinity, or inside $r=\frac{l}{1+e}$, in which case the electron falls towards the doublet.

The equation of the path is

$$\frac{l}{r}=1+e\cosh\left[C+\left(\frac{A'\cos\alpha}{\lambda}\right)^{\frac{1}{2}}\phi\right],$$

where C is constant.

The path is always open and no periodic orbits exist.

II. Motion on a Sphere.

From equations (1), (2), (3), p. 32, if we put $r=a$, where a is constant, we can derive the following equations:—

$$a^4\dot\theta^2=\mu a+2\lambda\cos\theta-\frac{h^2}{\sin^2\theta}, \quad \ldots \quad (1)$$

$$a^4\dot\theta^2=A+2\lambda\cos\theta-\frac{h^2}{\sin^2\theta}, \quad \ldots \quad (2)$$

$$a^2\sin^2\theta\dot\phi=h, \quad \ldots \quad (3)$$

where A and h are both constant.

The equations (1), (2) are identical if $A=\mu a$. Thus the equations of motion on the surface of the sphere give rise to the following two equations :—

$$a^4\dot{\theta}^2=\mu a+2\lambda\cos\theta-\frac{h^2}{\sin^2\theta}, \quad . \quad . \quad . \quad . \quad (4)$$

$$a^2\sin^2\theta\,\dot{\phi}=h. \quad . \quad . \quad . \quad . \quad . \quad . \quad (5)$$

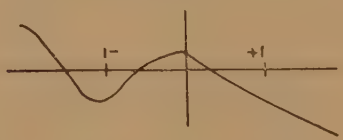
Putting $\cos\theta=x$, these equations become

$$a^4\left(\frac{dx}{dt}\right)^2=(\mu a+2\lambda x)(1-x^2)-h^2, \quad . \quad . \quad (6)$$

$$a^2(1-x^2)\frac{d\phi}{dt}=h. \quad . \quad . \quad . \quad . \quad . \quad (7)$$

Since the left-hand side of equation (6) is positive, the right-hand side must also be positive. Now, the right-hand side is a cubic polygonal in x ; if $x=-\infty$ the cubic is

Fig. 1.



positive ; if $x=-1$ the cubic is negative ; for some value of x between -1 and $+1$ the cubic must be positive ; when $x=+1$ the cubic is again negative ; and, lastly, when $x=+\infty$ the cubic is negative. The cubic has therefore two real roots between -1 and $+1$, and the third root is also real, but less than -1, so that it does not give a real value of θ.

Let the roots of the cubic be $\cos\alpha$, $\cos\beta$, and $-\cosh\gamma$, where $\cos\alpha>\cos\beta$.

The graphical representation of the cubic is as shown in the diagram (fig. 1).

Now, when

$$-\infty<x<-\cosh\gamma,$$

the cubic is positive but no real solution exists, for θ has no meaning ;

$$-\cosh\gamma<x<\cos\beta,$$

the cubic is negative and no real solution exists ;

$$\cos\beta<x<\cos\alpha,$$

the cubic is positive, in which case the motion is included between two cones of semi-vertical angles α and β respectively;

$$\cos\alpha < x < \infty,$$

the cubic is negative and no real solution exists.

Equation (6) can be put in the form

$$a^4\left(\frac{dx}{dt}\right)^2 = 2\lambda(\cos\alpha - x)(x - \cos\beta)(x + \cosh\gamma),$$

where
$$\cos\alpha + \cos\beta - \cosh\gamma = -\frac{\mu a}{2\lambda},$$

$$-\cos\alpha\cos\beta + \cos\alpha\cosh\gamma + \cos\beta\cosh\gamma = 1,$$

$$\cos\alpha\cos\beta\cosh\gamma = \frac{h^2 - \mu a}{2\lambda}.$$

We see here that the cases where μ is positive or negative are not separable.

The differential equation of the path is

$$\frac{1}{1-x^2}\frac{dx}{d\phi} = \frac{(2\lambda)^{\frac{1}{2}}}{h}\{(\cos\alpha - x)(x - \cos\beta)(x + \cosh\gamma)\}^{\frac{1}{2}}.$$

To integrate this equation put

$$x = \cos\alpha\cos^2\chi + \cos\beta\sin^2\chi,$$

where χ is a new variable.

With this substitution, the equation of the path is

$$\phi - \phi_0 = \frac{h}{\sqrt{2\lambda(\cosh\gamma + \cos\alpha)}}$$
$$\left[\frac{1}{1+\cos\alpha}\Pi\left(-\frac{\cos\alpha - \cos\beta}{1+\cos\alpha}, \sqrt{\frac{\cos\alpha - \cos\beta}{\cosh\gamma + \cos\alpha}}, \chi\right)\right.$$
$$+\frac{1}{1-\cos\alpha}\Pi\left(\frac{\cos\alpha - \cos\beta}{1-\cos\alpha}, \sqrt{\frac{\cos\alpha - \cos\beta}{\cosh\gamma + \cos\alpha}}, \chi\right)$$
$$-\frac{1}{1+\cos\alpha}\Pi\left(-\frac{\cos\alpha - \cos\beta}{1+\cos\alpha}, \sqrt{\frac{\cos\alpha - \cos\beta}{\cosh\gamma + \cos\alpha}}, \chi_0\right)$$
$$\left.-\frac{1}{1-\cos\alpha}\Pi\left(\frac{\cos\alpha - \cos\beta}{1-\cos\alpha}, \sqrt{\frac{\cos\alpha - \cos\beta}{\cosh\gamma + \cos\alpha}}, \chi_0\right)\right],$$

where ϕ_0 and χ_0 are the initial values of ϕ and χ.

In the special case when $\alpha=\beta$ the motion is on the intersection of a cone of which the semi-vertical angle is given by

$$\cos\alpha=-\frac{\mu a}{6\lambda}+\sqrt{\frac{\mu^2a^2}{36\lambda^2}+\frac{1}{3}}$$

with a sphere. The motion in this case is circular. The angular velocity of the electron is given by

$$\omega^2=\frac{\lambda}{a^4}\sec\alpha,$$

and h is given by

$$h=\pm a\sin^2\alpha\,\omega.$$

This case is that usually known as steady motion, discussed on p. 33.

Periodic Orbits.

Periodic orbits are formed on the surface of the sphere if

$$\frac{h}{\sqrt{2\lambda(\cosh\gamma+\cos\alpha)}}\frac{1}{1+\cos\alpha}\,\Pi\left(-\frac{\cos\alpha-\cos\beta}{1+\cos\alpha},\ \sqrt{\frac{\cos\alpha-\cos\beta}{\cosh\gamma+\cos\alpha}},\ k\pi\right)$$
$$+\frac{h}{\sqrt{2\lambda(\cosh\gamma+\cos\alpha)}}\frac{1}{1-\cos\alpha}\,\Pi\left(\frac{\cos\alpha-\cos\beta}{1-\cos\alpha},\ \sqrt{\frac{\cos\alpha-\cos\beta}{\cosh\gamma+\cos\alpha}},\ k\pi\right)=2n\pi,$$

where k and n are any positive integers.

Now, since

$$\cosh\gamma=\frac{1+\cos\alpha\cos\beta}{\cos\alpha+\cos\beta},$$
$$\frac{h}{\sqrt{2\lambda}}=\frac{\sin\alpha\sin\beta}{(\cos\alpha+\cos\beta)^{\frac{1}{2}}},$$

the condition for periodic orbits reduces to

$$\frac{\sin\alpha\sin\beta}{(1+2\cos\alpha\cos\beta+\cos^2\alpha)^{\frac{1}{2}}}\left[\frac{1}{1+\cos\alpha}\,\Pi\left(-\frac{\cos\alpha-\cos\beta}{1+\cos\alpha},\ \sqrt{\frac{\cos^2\alpha-\cos^2\beta}{1+2\cos\alpha\cos\beta+\cos^2\alpha}},\ k\pi\right)\right.$$
$$\left.+\frac{1}{1-\cos\alpha}\,\Pi\left(\frac{\cos\alpha-\cos\beta}{1-\cos\alpha},\ \sqrt{\frac{\cos^2\alpha-\cos^2\beta}{1+2\cos\alpha\cos\beta+\cos^2\alpha}},\ k\pi\right)\right]=2n\pi. \quad . \quad (8)$$

In the equation (8) k is a definite quantity which determines the order of the orbits.

In general, assuming that real solutions exist, we can represent $\cos\alpha$ to be measured on the x-axis, $\cos\beta$ to be measured on the y-axis, in rectangular Cartesian coordinates. Having done this, we can equate each side to z, where z is a third coordinate perpendicular to the plane xy. Hence we get

$$z=2n\pi, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (9)$$

$$z=\left[\frac{(1-x^2)(1-y^2)}{1+2xy+x^2}\right]^{\frac{1}{2}}\left\{\frac{1}{1+x}\right.$$

$$\Pi\left(-\frac{x-y}{1+x}, \sqrt{\frac{x^2-y^2}{1+2xy+x^2}}, k\pi\right)$$

$$\left.+\frac{1}{1-x}\Pi\left(\frac{x-y}{1-x}, \sqrt{\frac{x^2-y^2}{1+2xy+x^2}}, k\pi\right)\right\}. \quad . \quad (10)$$

For different positive integral values of n the equation (9) represents a series of planes, and for a given positive integral value of k the equation (10) represents a surface. The intersection of (8), (9) is a series of curves on which the condition (8) is satisfied. If this intersection is real, then periodic orbits exist on the surface of the sphere. (Owing to the difficulty of obtaining tables, the condition (8) cannot be actually verified.)

The time is given by

$$t+\epsilon=\sqrt{\frac{2}{\lambda(\cosh\gamma+\cos\alpha)}}\,a^2\mathrm{F}\left(\chi, \sqrt{\frac{\cos\alpha-\cos\beta}{\cosh\gamma+\cos\alpha}}\right),$$

where ϵ is constant.

III. General Motion.

The equations of motion are

$$\ddot{r}-r\dot{\theta}^2-r\sin^2\theta\dot{\phi}^2=-\frac{\mu}{r^2}-\frac{2\lambda\cos\theta}{r^3}, \quad . \quad . \quad (1)$$

$$\frac{1}{r}\frac{d}{dt}(r^2\dot{\theta})-r\sin\theta\cos\theta\dot{\phi}^2=-\frac{\lambda\sin\theta}{r^3}, \quad . \quad . \quad (2)$$

$$r^2\sin^2\theta\dot{\phi}=h. \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

From (1), (2), (3) we can derive the following equations:—

$$\dot{r}^2=\frac{2\mu}{r}-\frac{\mathrm{A}}{r^2}+\mathrm{B}, \quad . \quad . \quad . \quad . \quad . \quad . \quad (4)$$

$$r^4\dot{\theta}^2=\mathrm{A}+2\lambda\cos\theta-\frac{h^2}{\sin^2\theta}, \quad . \quad . \quad . \quad . \quad . \quad (5)$$

where A and B are constants.

By a similar reasoning to that when the motion is on a sphere, we can show that the motion is included between two cones of semi-vertical angles α and β, where $\cos\alpha$, $\cos\beta$, and $-\cosh\gamma$ are the roots of the cubic

$$A+2\lambda\cos\theta-\frac{h^2}{\sin^2\theta}=0.$$

Putting $\cos\theta=x$, we get the differential equations of the path to be

$$2\lambda(\cos\alpha-x)(x-\cos\beta)(x+\cosh\gamma)\left(\frac{du}{dx}\right)^2=2\mu u-Au^2+B, \quad \ldots \quad (6)$$

$$\left(\frac{d\phi}{dx}\right)^2=\frac{h^2}{2\lambda}\cdot\frac{1}{(1-x^2)^2(\cos\alpha-x)(x-\cos\beta)(x+\cosh\gamma)}. \quad (7)$$

The following cases are to be discussed separately :—

(*a*) A positive.

(*b*) A zero.

(*c*) A negative.

Case (*a*).—A positive.

(i.) μ positive.

The differential equations of the path are

$$\frac{2\lambda}{A}(\cos\alpha-x)(x-\cos\beta)(x+\cosh\gamma)\left(\frac{du}{dx}\right)^2=\frac{e^2}{l^2}-\left(u-\frac{1}{l}\right)^2,$$

$$\left(\frac{d\phi}{dx}\right)^2=\frac{h^2}{2\lambda}\cdot\frac{1}{(1-x^2)^2(\cos\alpha-x)(x-\cos\beta)(x+\cosh\gamma)},$$

where

$$\frac{e^2}{l^2}=\frac{B}{A}+\frac{\mu^2}{A^2},$$

$$\frac{\mu}{A}=\frac{1}{l},$$

$$\cos\alpha+\cos\beta-\cosh\gamma=-\frac{A}{2\lambda},$$

$$-\cos\alpha\cos\beta+\cos\alpha\cosh\gamma+\cos\beta\cosh\gamma=1,$$

$$\cos\alpha\cos\beta\cosh\gamma=\frac{h^2-A}{2\lambda}.$$

In the differential equations of the path put

$$x = \cos\alpha\cos^2\chi + \cos\beta\sin^2\chi;$$

then, after integrating, we get the equations of the path to be

$$\frac{l}{r} = 1 + e\cos\left[C + 2\sqrt{\frac{A}{2\lambda(\cosh\gamma+\cos\alpha)}}\,F\left(\chi, \sqrt{\frac{\cos\alpha-\cos\beta}{\cosh\gamma+\cos\alpha}}\right)\right],$$

$$\phi-\phi_0 = \frac{h}{\sqrt{2\lambda(\cosh\gamma+\cos\alpha)}}\left[\frac{1}{1+\cos\alpha}\Pi\left(-\frac{\cos\alpha-\cos\beta}{1+\cos\alpha}, \sqrt{\frac{\cos\alpha-\cos\beta}{\cosh\gamma+\cos\alpha}}, \chi\right)\right.$$

$$+\frac{1}{1-\cos\alpha}\Pi\left(\frac{\cos\alpha-\cos\beta}{1-\cos\alpha}, \sqrt{\frac{\cos\alpha-\cos\beta}{\cosh\gamma+\cos\alpha}}, \chi\right)$$

$$-\frac{1}{1+\cos\alpha}\Pi\left(-\frac{\cos\alpha-\cos\beta}{1+\cos\alpha}, \sqrt{\frac{\cos\alpha-\cos\beta}{\cosh\gamma+\cos\alpha}}, \chi_0\right)$$

$$\left.-\frac{1}{1-\cos\alpha}\Pi\left(\frac{\cos\alpha-\cos\beta}{1-\cos\alpha}, \sqrt{\frac{\cos\alpha-\cos\beta}{\cosh\gamma+\cos\alpha}}, \chi_0\right)\right],$$

where C is constant, ϕ_0 and χ_0 are the initial values of ϕ and χ.

Now, if $e < 1$, r oscillates between the maximum and minimum values given by $\frac{l}{1-e}$ and $\frac{l}{1+e}$ respectively.

If $e \geq 1$, then the maximum value of r is infinite and the path is always open.

Periodic Orbits.

The conditions for periodic orbits are :

(i.) $e < 1$ (this makes the value of r oscillatory);

(ii.) $$\sqrt{\frac{1-\cos^2\alpha-\cos^2\beta-\cos\alpha\cos\beta}{1+2\cos\alpha\cos\beta+\cos^2\alpha}}\,F\left(k\pi, \sqrt{\frac{\cos^2\alpha-\cos^2\beta}{1+2\cos\alpha\cos\beta+\cos^2\alpha}}\right) = m\pi;$$

(iii.) $$\frac{\sin\alpha\sin\beta}{(1+2\cos\alpha\cos\beta+\cos^2\alpha)^{\frac{1}{2}}}\left[\frac{1}{1+\cos\alpha}\right.$$
$$\Pi\left(-\frac{\cos\alpha-\cos\beta}{1+\cos\alpha}, \sqrt{\frac{\cos^2\alpha-\cos^2\beta}{1+2\cos\alpha\cos\beta+\cos^2\alpha}}, k\pi\right)$$
$$+\frac{1}{1-\cos\alpha}\Pi\left(\frac{\cos\alpha-\cos\beta}{1-\cos\alpha}, \sqrt{\frac{\cos^2\alpha-\cos^2\beta}{1+2\cos\alpha\cos\beta+\cos^2\alpha}}, k\pi\right)\Big] = 2n\pi,$$

where k, m, n are any positive integers.

In equations (ii.), (iii.), k is a definite quantity which determines the order of the orbits.

In general, assuming that real solutions exist, we can represent $\cos\alpha$ to be measured along the x-axis, $\cos\beta$ to be measured along the y-axis in rectangular Cartesian coordinates. Having done this we can equate each side to z, where z is a third coordinate perpendicular to the plane of xy. Hence we get

$$z = m\pi, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (8)$$

$$z = \left(\frac{1-x^2-y^2-xy}{1+2xy+x^2}\right)^{\frac{1}{2}} \mathrm{F}\left(k\pi, \sqrt{\frac{x^2-y^2}{1+2xy+x^2}}\right), \quad . \quad (9)$$

$$z = 2n\pi, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (10)$$

$$z = \left[\frac{(1-x^2)(1-y^2)}{1+2xy+x^2}\right]^{\frac{1}{2}}$$
$$\left[\frac{1}{1+x}\Pi\left(-\frac{x-y}{1+x}, \sqrt{\frac{x^2-y^2}{1+2xy+x^2}}, k\pi\right)\right.$$
$$\left.+\frac{1}{1-x}\Pi\left(\frac{x-y}{1+x}, \sqrt{\frac{x^2-y^2}{1+2xy+x^2}}, k\pi\right)\right]. \quad (11)$$

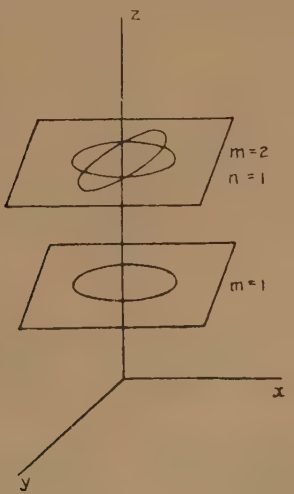
For any given positive integral value of k the equations (9), (11) represent two surfaces ; and for different positive integral values of m, n the equations (8), (10) represent the two series of planes. The intersections of (8), (9) are a series of curves on which the condition (ii.) is satisfied ; similarly the intersections of (10), (11) are a series of curves on which the condition (ii.) is satisfied. The graphical representation of these conditions is as shown in the diagram (fig. 2).

The points which give solution for periodic orbits are :—

(*a*) The points of intersection of the curves for which $m = 2n$.

(*b*) Take any point on one of the "m" curves (*i. e.* 8, 9), draw a straight line from this point parallel to the z-axis; then if this straight line intersects one or more of the "n" curves (*i. e.* 10, 11), the values of $\cos\alpha$, $\cos\beta$ obtained is a solution for periodic orbits. This is simply because the point on the "m" curve and the points of intersection of the straight line through this point and parallel to the z-axis with the "n" curves give the same value of $\cos\alpha$, $\cos\beta$. In other words, project all the "n" curves on to the plane of any one of the "m" curves; then the points of intersection of this "m" curve and the projection of the "n" curves give solutions for periodic orbits.

Fig. 2.



It will be noticed that (*a*) is included in (*b*). (Owing to the difficulty of obtaining tables, the conditions (ii.) and (iii.) cannot actually be verified.)

(ii.) μ negative.

In equations (6), (7), p. 44, put $\mu=-\mu'$, where μ' is positive. These equations become

$$\frac{2\lambda}{A}(\cos\alpha-x)(x-\cos\beta)(x+\cosh\gamma)\left(\frac{du}{dx}\right)^2=\frac{e^2}{l^2}-\left(u+\frac{1}{l}\right)^2,$$

$$\left(\frac{d\phi}{dx}\right)^2=\frac{h^2}{2\lambda}\cdot\frac{1}{(1-x^2)^2(\cos\alpha-x)(x-\cos\beta)(x+\cosh\gamma)}.$$

In this case, e must be greater than 1 for a real solution to exist. The maximum of r is infinite and the minimum value is $\frac{l}{e-1}$. In this case no periodic orbits exist.

The equations of the path are

$$\frac{l}{r} = -1 + e\cos\left[\mathrm{C} + 2\sqrt{\frac{\mathrm{A}}{2\lambda(\cosh\gamma+\cos\alpha)}}\,\mathrm{F}\left(\chi, \sqrt{\frac{\cos\alpha-\cos\beta}{\cosh\gamma+\cos\alpha}}\right)\right],$$

$$\phi + \mathrm{D} = \frac{h}{\sqrt{2\lambda(\cosh\gamma+\cos\alpha)}}\left[\frac{1}{1+\cos\alpha}\Pi\left(-\frac{\cos\alpha-\cos\beta}{1+\cos\alpha}, \sqrt{\frac{\cos\alpha-\cos\beta}{\cosh\gamma+\cos\alpha}}, \chi\right) + \frac{1}{1-\cos\alpha}\Pi\left(\frac{\cos\alpha-\cos\beta}{1-\cos\alpha}, \sqrt{\frac{\cos\alpha-\cos\beta}{\cosh\gamma+\cos\alpha}}, \chi\right)\right],$$

where C and D are constants and $\cos\alpha$, $\cos\beta$, and $-\cosh\gamma$ have the same meaning as when μ is positive.

Case (b).—A = zero.

(i.) μ positive.

The differential equations of the path are

$$2\lambda(\cos\alpha - x)(x-\cos\beta)(x+\cosh\gamma)\left(\frac{du}{dx}\right)^2 = 2\mu u + \mathrm{B},$$

$$\left(\frac{d\phi}{dx}\right)^2 = \frac{h^2}{2\lambda}\cdot\frac{1}{(1-x^2)^2(\cos\alpha - x)(x-\cos\beta)(x+\cosh\gamma)},$$

where $\cos\alpha$, $\cos\beta$, and $-\cosh\gamma$ are connected by the relations

$$\cos\alpha + \cos\beta - \cosh\gamma = 0,$$

$$-\cos\alpha\cos\beta + \cos\alpha\cosh\gamma + \cos\beta\cosh\gamma = 1,$$

$$\cos\alpha\cos\beta\cosh\gamma = \frac{h^2}{2\lambda}.$$

If B is positive, the electron goes to infinity if projected away from the origin, and goes to the origin if projected towards it. Thus the path in this case is always open.

Putting

$$x = \cos\alpha\cos^2\chi + \cos\beta\sin^2\chi,$$

the equations of the path are

$$\frac{4\lambda}{\mu}\cdot\frac{1}{r}+\frac{2\lambda B}{\mu^2}=\left[C+2\sqrt{\frac{1}{\cosh\gamma+\cos\alpha}}\,F\left(\chi,\sqrt{\frac{\cos\alpha-\cos\beta}{\cosh\gamma+\cos\alpha}}\right)\right]^2,$$

$$\phi+D=\frac{h}{\sqrt{2\lambda(\cosh\gamma+\cos\alpha)}}\left[\frac{1}{1+\cos\alpha}\Pi\left(-\frac{\cos\alpha-\cos\beta}{1+\cos\alpha},\sqrt{\frac{\cos\alpha-\cos\beta}{\cosh\gamma+\cos\alpha}},\chi\right)+\frac{1}{1-\cos\alpha}\Pi\left(\frac{\cos\alpha-\cos\beta}{1-\cos\alpha},\sqrt{\frac{\cos\alpha-\cos\beta}{\cosh\gamma+\cos\alpha}},\chi\right)\right],$$

where C and D are constants.

If B is negative, then r passes through the maximum value $\frac{2\mu}{B'}$, where $B=-B'$; thus the electron goes to the origin if projected away from or towards the origin. The equations of the path are as when B is positive, if we put $B=-B'$, where B' is positive.

(ii.) μ negative.

Put $\mu=-\mu'$, where μ' is positive.
The differential equations of the path are

$$2\lambda(\cos\alpha-x)(x-\cos\beta)(x+\cosh\gamma)\left(\frac{du}{dx}\right)^2=-2\mu' u+B,$$

$$\left(\frac{d\phi}{dx}\right)^2=\frac{h^2}{2\lambda}\cdot\frac{1}{(1-x^2)^2(\cos\alpha-x)(x-\cos\beta)(x+\cosh\gamma)}.$$

In this case B must be positive. Thus r passes through the minimum value $\frac{2\mu'}{B}$. The path is always open.

The equations of the path are

$$\frac{4\lambda}{\mu'}\cdot\frac{1}{r}=\frac{2\lambda B}{\mu'^2}-\left[C+\frac{2}{\sqrt{\cosh\gamma+\cos\alpha}}\,F\left(\chi,\sqrt{\frac{\cos\alpha-\cos\beta}{\cosh\gamma+\cos\alpha}}\right)\right]^2,$$

$$\phi+\mathrm{D}=\frac{h}{\sqrt{2\lambda(\cosh\gamma+\cos\alpha)}}$$
$$\left[\frac{1}{1+\cos\alpha}\Pi\left(-\frac{\cos\alpha-\cos\beta}{1+\cos\alpha},\sqrt{\frac{\cos\alpha-\cos\beta}{\cosh\gamma+\cos\alpha}},\chi\right)\right.$$
$$\left.+\frac{1}{1-\cos\alpha}\Pi\left(\frac{\cos\alpha-\cos\beta}{1-\cos\alpha},\sqrt{\frac{\cos\alpha-\cos\beta}{\cosh\gamma+\cos\alpha}},\chi\right)\right],$$

where C and D are constants.

Case (*c*).—A negative.

Put $\mathrm{A}=-\mathrm{A}'$, where A′ is positive.
The differential equations of the path are

$$2\lambda(\cos\alpha-x)(x-\cos\beta)(x+\cosh\gamma)\left(\frac{du}{dx}\right)^2=2\mu u+\mathrm{A}'u^2+\mathrm{B},$$

$$\left(\frac{d\phi}{dx}\right)^2=\frac{h^2}{2\lambda}\frac{1}{(1-x^2)^2(\cos\alpha-x)(x-\cos\beta)(x+\cosh\gamma)}.$$

(i.) μ positive.

If $\frac{\mathrm{B}}{\mathrm{A}'}-\frac{\mu^2}{\mathrm{A}'^2}$ is positive, the electron goes to infinity if projected away from the origin, but goes to the origin if projected towards it. Thus the path is always open.
The equations of the path are

$$\frac{l}{r}=e\sinh\left[\mathrm{C}+2\sqrt{\frac{\mathrm{A}'}{2\lambda(\cosh\gamma+\cos\alpha)}}\,\mathrm{F}\left(\chi,\sqrt{\frac{\cos\alpha-\cos\beta}{\cosh\gamma+\cos\alpha}}\right)\right]-1,$$

$$\phi+\mathrm{D}=\frac{h}{\sqrt{2\lambda(\cosh\gamma+\cos\alpha)}}$$
$$\left[\frac{1}{1+\cos\alpha}\Pi\left(-\frac{\cos\alpha-\cos\beta}{1+\cos\alpha},\sqrt{\frac{\cos\alpha-\cos\beta}{\cosh\gamma+\cos\alpha}},\chi\right)\right.$$
$$\left.+\frac{1}{1-\cos\alpha}\Pi\left(\frac{\cos\alpha-\cos\beta}{1-\cos\alpha},\sqrt{\frac{\cos\alpha-\cos\beta}{\cosh\gamma+\cos\alpha}},\chi\right)\right],$$

. . . (12)

where C and D are constants.

$$\cos\alpha+\cos\beta-\cosh\gamma=\frac{A'}{2\lambda},$$

$$-\cos\alpha\cos\beta+\cos\alpha\cosh\gamma+\cos\beta\cosh\gamma=1,$$

$$\cos\alpha\cos\beta\cosh\gamma=\frac{h^2+A'}{2\lambda},$$

$$x=\cos\alpha\cos^2\chi+\cos\beta\sin^2\chi.$$

If $B=\frac{\mu'}{A'}$, the path is always open.

The equations of the path are

$$\log\left(\frac{1}{r}-\frac{\mu}{A'}\right)=C+2\sqrt{\frac{A'}{2\lambda(\cosh\gamma+\cos\alpha)}}\,F\left(\chi,\sqrt{\frac{\cos\alpha-\cos\beta}{\cosh\gamma+\cos\alpha}}\right),$$

and the equation (12).

If $\frac{B}{A'}-\frac{\mu^2}{A'^2}$ is negative, r passes through the maximum value $\frac{l}{e-1}$. If $e>1$ is greater than unity, the electron falls towards the doublet, but if e is less than unity, the electron goes to infinity when projected away from the origin, but goes to the origin when projected towards it.

The equations of the path are

$$\frac{l}{r}=e\cosh\left[C+2\sqrt{\frac{A'}{2\lambda(\cosh\gamma+\cos\alpha)}}\,F\left(\chi,\sqrt{\frac{\cos\alpha-\cos\beta}{\cosh\gamma+\cos\alpha}}\right)\right]-1,$$

and the equation (12).

(ii.) μ negative.

Put $\mu=-\mu'$, where μ' is positive.

If $\frac{B}{A'}-\frac{\mu'^2}{A'^2}$ is positive, the electron goes to infinity when projected away from the origin, but goes to the origin when projected towards it. Thus the path is always open.

The equations of the path are

$$\frac{l}{r} = 1 + e \sinh \left[C + 2 \sqrt{\frac{A'}{2\lambda(\cosh\gamma + \cos\alpha)}} \, F\left(\chi, \sqrt{\frac{\cos\alpha - \cos\beta}{\cosh\gamma + \cos\alpha}}\right)\right],$$

and equation (12), where C is constant.

If $B = \frac{\mu'}{A'}$, the path is always open.

The equations of the path are

$$\log\left(\frac{1}{r} - \frac{\mu'}{A'}\right) = C + 2 \sqrt{\frac{A'}{2\lambda(\cosh\gamma + \cos\alpha)}} \, F\left(\chi, \sqrt{\frac{\cos\alpha - \cos\beta}{\cosh\gamma + \cos\alpha}}\right),$$

and equation (12), where C is constant.

If $\frac{B}{A'} - \frac{\mu'^2}{A'^2}$ is negative, then r either passes through the maximum value $\frac{l}{1+e}$ or the minimum value $\frac{l}{1-e}$. In the former case the electron falls towards the doublet, and in the latter case it goes to infinity. Thus the path is always open.

The equations of the path are

$$\frac{l}{r} = 1 + e \cosh \left[C + 2 \sqrt{\frac{A'}{2\lambda(\cosh\gamma + \cos\alpha)}} \, F\left(\chi, \sqrt{\frac{\cos\alpha - \cos\beta}{\cosh\gamma + \cos\alpha}}\right)\right],$$

and equation (12), where C is constant.

The author wishes to express his thanks to Prof. S. Brodetsky of Leeds University, under whose supervision the above work was done.

IV. *On the Change that a Gaseous Molecule may undergo between two Consecutive Collisions.* *By* R. D. Kleeman, *B.A., D.Sc.* *.

§ 1. *Introductory Remarks.*

In a previous paper † the writer has shown that strictly according to thermodynamics the equation of a perfect gas is

$$pv = \xi MRT, \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

where p denotes the pressure of a mass of M mols at the volume v and absolute temperature T, and ξ a function of the quantities T, v, and M. Under ordinary conditions the quantity ξ differs inappreciably from unity, but is less than unity when v is very large, as will be shown in § 2.

A consequence of this result and a previous investigation on the constant of mass action ‡ is that this constant under all conditions is likely to be appreciably a function of the volume and masses of the constituents as well as of the temperature, when the volume is very large. A corollary of this result is that a molecule during collision undergoes a physical and chemical change, or activation, which gradually disappears, on account of which the constant of mass action varies in this manner. In a subsequent article § some experimental evidence of this activation is discussed, which is shown, for example, by the effect of pressure on the spectrum of a gas. Another consequence of equation (1) is that contact catalytic action is likely to exist. The evidence in favour of this seems overwhelming, and will be considered in a separate article. In this paper the physical significance of the function ξ will be investigated.

§ 2. *The Function ξ Decreases as v Increases.*

On substituting in the well-known thermodynamical equation

$$\frac{\partial u}{\partial v} = T\frac{\partial p}{\partial T} - p \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

for p from equation (1), it becomes

$$\frac{\partial u}{\partial v} = MR\frac{T}{v}\frac{\partial \xi}{\partial T}, \quad . \quad . \quad . \quad . \quad . \quad (3)$$

* Communicated by the Author.
† Phil. Mag. v. p. 1191 (1928).
‡ Phil. Mag. v. p. 263 (1928).
§ 'Science,' lxviii. 1767, p. 459 (1928).

where u denotes the internal energy at the volume v and temperature T. On multiplying this equation by ∂v and integrating it between the limits ∞ and v, we obtain

$$u_\infty - u_v = \mathrm{MR}\int_v^\infty \frac{\mathrm{T}}{v}\frac{\partial \xi}{\partial \mathrm{T}}\cdot \partial v, \quad . \quad . \quad . \quad . \quad (4)$$

where u_∞ and u_v denote the internal energies of the gas at the volumes ∞ and v respectively. We may express ξ in the form of a sum of products of functions of T and v, or write

$$\xi = \Sigma \phi_1(\mathrm{T}) \cdot \phi_2(v) \ldots \quad . \quad . \quad . \quad . \quad . \quad (5)$$

Each of the functions ϕ_2 may be expanded in a series of powers of v, or we may write

$$\phi_2(v) = \Sigma \frac{\mathrm{A}}{v^\alpha}, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (6)$$

where α is a quantity at present unrestricted.

It is obvious that the left-hand side of equation (4) cannot be infinite. Therefore, if we substitute in the equation for ξ from equations (5) and (6), it appears that α can have only positive values integral or fractional. *It follows, therefore, that ξ decreases as v increases.* Another thermodynamical method of proving the existence of the function ξ and its properties will be given in § 5.

§ 3. *The Velocity of a Molecule in a Gas changes between two Consecutive Collisions.*

The function ξ, we have seen, decreases as v increases. On reflexion it will appear that this effect can be explained only by a decrease in the average velocity of translation of the molecules with increase of v. To see how this may come about, consider a rarefied gas from which some molecules are removed, keeping the volume constant. A decrease in the number of collisions per second, and in the velocity of translation of the molecules, simultaneously takes place, and hence we must look for an association between these two effects. If the velocity between two consecutive collisions of a molecule remained constant, the average velocity of the molecules would not decrease with the decrease in volume, or with decrease in the number of collisions. Hence we conclude that the velocity of a molecule gradually decreases after a collision, and that the subsequent collision increases it again to its initial value. The average velocity of the molecules will accordingly decrease with increase of volume.

The increase in velocity of a molecule during collision with another molecule can evidently take place only at the expense of the liberation of molecular internal energy, which has an effect resembling an explosion between the colliding molecules. This effect is appreciable only when the concentration is very small. Under ordinary conditions the change in the velocity of a molecule between two consecutive collisions, and the corresponding internal energy liberated, is inappreciable. The concentration at which this no longer holds must be determined by experiment (§ 6).

In general we may accordingly write

$$V_a - V_b = \phi(t), \quad . \quad . \quad . \quad . \quad . \quad . \quad (7)$$

where V_b denotes the velocity of a molecule before and V_a after collision, and t the time between two consecutive collisions. When t has a value smaller than that corresponding to a gas exceptionally rarefied, $\phi(t)$ is practically zero, and hence $V_a - V_b = 0$, approximately.

The value of V_a under the foregoing conditions is approximately that given by the equation

$$V_a = \sqrt{\frac{3RT}{m}}, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (8)$$

derived from the orthodox gas theory, where m denotes the molecular weight of the gas. It may also hold in general down to the smallest concentrations, but it is scarcely likely; no theoretical prediction can be made at present in regard to this point. It may be pointed out that $V_a - V_b$ may be as small as we please, if the average velocity differs by an appropriate amount from that given by equation (8).

§ 4. *The Effect of Heat Radiation on the Molecular Velocity of Translation.*

The molecules of a gas cannot go on expending some of their internal energy while undergoing collisions without replenishing from some source. This, it seems, can be no other than the heat radiation surrounding the molecules. It is not difficult to conceive a process by means of which this replenishing may be brought about. The parts of two molecules nearest to each other during a collision most likely furnish the internal energy necessary to increase the molecular velocity after collision. These parts are therefore likely to be in a condition (after collision) to absorb radiant energy from the surrounding space, or to absorb more

energy than they emit. In this manner the internal energy expended during a collision may wholly or partly be replenished in the interval between two consecutive collisions.

The parts diametrically opposite to the foregoing parts of two colliding molecules are in equilibrium with the surrounding radiation, and therefore they reflect as much radiation as they absorb. The pressure of the radiation on these parts would therefore be greater than on the former parts which absorb more than they reflect. The molecules would accordingly slow down under these opposing radiation pressures of different magnitudes. Thus the process that replenishes the internal energy expended during collision also gives rise to a decrease in the molecular velocity.

The average molecular velocity after a collision, or the average value of V_a, similarly as the total average velocity, probably depends on the molecular concentration as well as on the temperature, as has already been pointed out, and most likely decreases with decrease of concentration.

It can easily be shown that in general the radiation surrounding a molecule will affect its velocity of translation. Thus consider a molecule in equilibrium with the surrounding radiation, and suppose that its velocity, according to the orthodox view, remains unaltered when not undergoing a collision. Now suppose that the radiation surrounding the molecules is changed correspondingly to a different temperature. If the absorption and the reflexion of the heat radiation by the molecules are each changed by the same multiple over each part of the surface of the molecules, their average velocity of translation will remain unaltered. But since the average velocity is changed correspondingly to the temperature, it follows that the absorption and reflexion are changed in a way that each molecule is subjected to an asymmetrical radiation pressure which either increases or decreases its velocity, as the case may be. The corresponding radiant energy absorbed or emitted by the molecule per unit change in temperature, it may be pointed out, represents the internal molecular specific heat.

§ 5. *Another Method of deducing Equation* (1).

The effect of the pressure of a gas on its spectrum, and the effect of the concentration of a salt in a flame on its spectrum, shows that a molecule undergoes a physical change during collision which gradually disappears. This experimental fact will be used to deduce equation (1).

The foregoing change must necessarily be associated with a change in internal molecular energy, and hence the internal energy of a gas depends on its volume, or $\frac{\partial u}{\partial v}$ is not zero, where u denotes its internal energy. It follows, then, from equation (3) that ξ is a function of T. On completing the integration of equation (4), supposing ξ a function of T only, we obtain

$$u_\infty - u_v = \mathrm{MRT}\frac{\partial \xi}{\partial \mathrm{T}}\left\{\log \infty - \log v\right\} \quad . \quad . \quad (9)$$

where u_∞ and u_v denote the internal energies of a gas at the volumes ∞ and v respectively. The right-hand side of the equation is infinite, and this should therefore also hold for the left-hand side. But this is impossible ; and ξ is therefore a function of v as well as of T, which on integration of equation (4) renders the right side of the equation finite. This establishes equation (1) along a different line* of reasoning than before, and places its truth beyond doubt.

* In a letter (Phil. Mag. vi. p. 743, 1928) the writer pointed out a thermodynamical proof of equation (1) which does not depend on the zero of entropy. Since this equation is of great importance, especially in connexion with mass-action, a complete outline of the proof will be given here. On writing Clapeyron's equation in the form

$$p(v_2 - v_1) = \mathrm{L}\cdot\frac{p}{\mathrm{T}\dfrac{dp}{d\mathrm{T}} - p},$$

the factor of L assumes an indeterminate form when T=0 and p=0, whose value is, however, finite and may be obtained by successive differentiations (J. Frank. Inst. 206 (5), p. 691, 1928). Therefore at T=0 we have L=0, since $p(v_2 - v_1) = \mathrm{RT} = 0$. Now, suppose that a substance initially at T=0 under its vapour pressure is passed through the following cycle: (*a*) evaporate the substance, (*b*) raise the temperature of the vapour to T_m, (*c*) condense the vapour, (*d*) lower the temperature of the substance in contact with its vapour to T=0. On equating the change in internal energy to zero, and remembering that L=0, we obtain (*loc. cit.*)

$$\mathrm{C}_\infty = \mathrm{C} + \frac{\mathrm{L}_m}{\mathrm{T}_m},$$

where L_m denotes the internal heat of evaporation at T_m, and C_∞ and C denote the average internal specific heats of the vapour and liquid respectively. Now it follows from thermodynamics that the scale of the perfect gas thermometer and the thermodynamical scale coincide if the ratio γ of the specific heats of the gas is a constant. But this does not hold for any substance according to the foregoing expression for C_∞, since $\mathrm{L}_m/\mathrm{T}_m$ has a large maximum value when T_m is small. Hence if the scale of the gas thermometer is expressed in terms of the thermodynamical scale, equation (1) is obtained, where ξ is a function of the thermodynamical temperature T. It can then be shown from equation (9) in §5 that it is also a function of the volume.

§ 6. *Experimental Methods of investigating the Nature of the Function* ξ.

The molecular concentration at which ξ begins to differ appreciably from unity cannot be predicted theoretically, but is probably extremely small. This point might be experimentally investigated by measuring the pressure of a rarefied gas by means of a device involving the velocity of molecular translation in its pressure formula, and comparing it with the pressure indicated by a device which measures the mass of a given volume of gas. A device of the latter kind is the McLeod gauge, but one of its drawbacks is that it cannot be used for very low pressures on account of the vapour-pressure of mercury. An ionization gauge might be found more convenient to use. The constants of both devices might be determined corresponding to a given pressure or pressures. On applying both devices to the measurement of the pressure of a rarefied gas which is gradually decreased by steps, a point will ultimately be reached when the pressure indicated by the device involving the velocity of molecular translation indicates a smaller value than the other. This point corresponds to the concentration at which ξ begins to deviate appreciably from unity. It will probably be found to depend on the nature of the gas.

§ 7. *Miscellaneous Deductions.*

(*a*) The exact form of the equation of state of a substance which conforms to equation (1) cannot be predicted theoretically at present. But forms may be suggested that might conceivably represent the facts. One of them referring to one mol is

$$p=\frac{\mathrm{RTA}}{v(v\alpha+1)}+\Sigma\frac{\mathrm{B}_\alpha}{v^{2+\alpha}}, \quad . \quad . \quad . \quad . \quad . \quad (10)$$

where α is a positive quantity equal to or greater than zero, and A, α, B_α are functions of T. Let us suppose that α is a very small fraction, say, of the order 10^{-5}, that A differs inappreciably from unity, and that B_α has values which render the summation expression in the equation negligible in comparison with the preceding term when v has values (per mol) corresponding to a gas under ordinary conditions. The equation of state of a gas under ordinary conditions is then

$$p=\frac{\mathrm{RT}}{v}, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (11)$$

very approximately according to the foregoing equation,

which agrees with experiment. When, however, the volume is infinitely large, the equation of state assumes the form

$$p=\left(\frac{\mathrm{RTA}}{a}+\mathrm{B}_1\right)\frac{1}{v^2}, \quad . \quad . \quad . \quad . \quad . \quad . \quad (12)$$

according to which the pressure varies inversely as the square of the volume. The expression for ξ, according to equation (10), is therefore

$$\xi=\frac{\mathrm{A}}{av+1}+\frac{\mathrm{B}_1}{\mathrm{RT}v}. \quad . \quad . \quad . \quad . \quad . \quad . \quad (13)$$

If we substitute for p in equation (2) from equation (10), multiply it by ∂v and integrate it between the limits of v and ∞, where v refers to a gas under ordinary conditions, it can easily be shown that very approximately

$$u_\infty-u_v=\mathrm{T}^2\frac{\partial}{\partial \mathrm{T}}\left\{\mathrm{RA}\ln\left(\frac{av+1}{av}\right)+\frac{\mathrm{B}_1}{\mathrm{T}v}\right\} \quad . \quad . \quad (14)$$

The right-hand side is not infinite so far as the dependence of u on v is concerned, as should be the case since the left-hand side cannot be infinite.

(*b*) When a gas is very rarefied, the only force operating between the molecules is gravitational attraction. Now, Mills * has shown that when two molecules attract each other with a force varying inversely as the square of their distance of separation, the work w done in separating the molecules of a gram of substance at the volume v so that its volume is finally infinite, is given by

$$w=\frac{\mathrm{D}}{v^{1/3}}, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (15)$$

where D is a constant. The intrinsic pressures P_n at the volume v, or the negative pressure due to the attraction of the molecules upon each other, is given by

$$\mathrm{P}_n=-\frac{\partial w}{\partial v}, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (16)$$

and hence

$$\mathrm{P}_n=\frac{\mathrm{D}}{3v^{4/3}}. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (17)$$

The pressure p_t due to the motion of translation of the molecules is given by

$$p_t=\frac{\mathrm{RT}}{v}, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (18)$$

* J. Phys. Chem. viii. p. 383 (1904).

according to the orthodox view, and hence the pressure p actually exerted by the gas is

$$p_t - P_n = \frac{RT}{v} - \frac{D}{3v^{4/3}} \quad . \quad . \quad . \quad . \quad . \quad (19)$$

Now, under ordinary conditions p_t is large in comparison with P_n, and this will still be the case however large the volume according to the right-hand side of the foregoing equation. Hence, if this equation were to hold, a mass of gas in interstellar space would continue to expand till evenly distributed.

But if p_t is given by equation (1), this may not take place. For example, if the pressure due to the motion of translation of the molecules of a gas whose volume is large is given by equation (12), it will follow that for a certain large volume $p_t - P_n$ is zero, and the gas will then cease to expand *as a whole* if left to itself. Under these conditions a gas in interstellar space would move like a solid body. These considerations may be of importance in interpreting the distribution and behaviour of masses of rarefied gases in interstellar space.

(*c*) It will be evident that Maxwell's law of distribution of molecular velocities holds only for a gas in which the velocities of translation of each molecule between two consecutive collisions does not change. When this no longer holds, the law has to be replaced by an appropriately modified form.

§ 8. *Applications to an Electron Gas.*

The case of an electron gas, or mass of matter consisting of electrons, requires special investigation. Consider a mass of electrons whose volume is increased till it is infinitely large, keeping the temperature at the absolute zero. The internal energy will evidently reach a limiting minimum value. According to a previous investigation *, this state corresponds to the zero of the controllable internal energy of the mass of electrons. It was also shown † that this zero lies on the adiabatic of zero controllable entropy. This particular adiabatic can be shown to correspond to $T=0$, since, according to our fundamental notions of heat, the specific heat is a positive quantity ‡, and hence an increase in temperature from $T=0$ will give rise to an increase in entropy. Therefore, if L denote the increase in internal

* Phil. Mag. iii. p. 888 (1927).
† *Loc. cit.* iv. p. 261 (1927).
‡ *Loc. cit.* v. p. 668 (1928).

energy and w the external work done on expanding the mass of electrons from the volume v to ∞ at $T=0$, we have

$$\frac{L+w}{T}=0. \quad . \quad . \quad . \quad . \quad . \quad . \quad (20)$$

Now,

$$L+w=T\int_v^\infty \frac{\partial p}{\partial T}\cdot \partial v, \quad . \quad . \quad . \quad . \quad . \quad (21)$$

according to equation (2), and hence, on combining the two equations, we have

$$\int_v^\infty \frac{\partial p}{\partial T}\cdot \partial v=0 \quad . \quad . \quad . \quad . \quad . \quad . \quad (22)$$

at $T=0$.

The equation of state of a mass of gaseous electrons may be written

$$p=p_t-P_n, \quad . \quad . \quad . \quad . \quad . \quad . \quad (23)$$

where p_t denotes the pressure the electrons exert due to their motion of translation, and P_n the intrinsic pressure due to the repulsion between the electric charges. p_t is given by equation (1) and P_n by equation (17) on changing the sign of the right-hand side, and the equation may therefore be written

$$p=\frac{RT\xi}{v}+\frac{D}{3v^{4/3}}. \quad . \quad . \quad . \quad . \quad . \quad (24)$$

On substituting from this equation for p in equation (22), it becomes

$$\frac{\partial}{\partial T}\left\{RT\int_v^\infty \frac{\xi}{v}\cdot \partial v\right\}=0. \quad . \quad . \quad . \quad (25)$$

Thus, unless ξ is an appropriate function of T, the left-hand side will not be zero. It can then be shown similarly, as in § 5, that ξ is also a function of v.

The various deductions made for an ordinary gas therefore also apply with slight modifications to an electron gas. One which is of particular interest is that an electron, like an atom, is *continually changing in nature*, though these changes may, of course, be immeasurably small. It appears, therefore, that the Universe has not only been evolving in respect to its shape and its animal and plant-life, but also in respect to the primordial electron and atom. That is perhaps just what we might expect. This aspect of the results obtained will be discussed in a special article.

An electron, like a molecule, undergoes a decrease in velocity between two consecutive collisions. But the

process by means of which this is brought about is likely to be different in the two cases. When an electron absorbs radiant energy, this is likely to appear mainly as kinetic energy of translation. Let us suppose that this is so, and consider what happens when an electron is subjected to an alternating electric field. If the electron is moving parallel to the field with a velocity of its own, more work is done upon it when the field is acting in the same direction than when acting in the opposite direction. The electron would accordingly continually increase in velocity. This takes place also if the electron is subjected to fields whose axes lie in different directions, such as are furnished by the heat radiation surrounding it. But the velocity cannot continually increase, and therefore the force exerted on an electron by an electric field in the same direction as it is moving is less than when the field is acting in the opposite direction. Furthermore, since the electron should actually slow down if left to itself, the relation between these forces is such that this is brought about.

But the electron must also change in internal electronic energy, since its velocity is increased by a collision at the expense of this energy. It is difficult to see how this may be brought about according to our present knowledge of electricity. The electron is evidently, after all, an entity of some complexity; in fact, it seems safe to predict that it will be found very much so when we get to know a good deal more about its properties. These will be further investigated thermodynamically in connexion with radiation in a paper that will appear shortly.

§ 9. *Application to Carnot's Cycle.*

Since the laws of thermodynamics are, as far as we know, independent of the nature of matter, they will not be violated by a continuous change in the nature of matter with time, which the writer has predicted *, however great or small the change may be.

If Q_1 denote the heat taken in at the temperature T_1 in passing a substance through a Carnot's cycle, and Q_2 the heat given out at temperature T_2, the substance may repeatedly be passed through a cycle in which Q_1, Q_2, T_1, and T_2 have the same values. Since the substance continually changes in nature during the process, it is never the same as before at a point where an isothermal and an adiabatic curve of a

* Phil. Mag. v. p. 1191 (1928).

cycle meet. Its internal energy need not be always the same either at such a point. But since the system as a whole may not continually loose or gain internal energy, the state corresponding to a given value of the internal energy is passed to a different point during each cycle without violating its thermodynamical laws.

But this and other changes that take place in the physical properties of the substance, as may again be pointed out, are so small that they are of no practical importance ; in fact, they are probably so small that they cannot be measured. The same remarks apply to the continual changes that take place in the chemical properties of a substance. But temporary changes may be induced in the atoms of a substance which give rise to a temporary and exceptionally pronounced departure in the chemical behaviour, as shown by the phenomenon of catalytic action.

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V. *The Limiting Density in White Dwarf Stars.* *By* Edmund C. Stoner, *Ph.D.* (*Cambridge*), *Reader in Physics, University of Leeds* *.

Introduction.

A NUMBER of stars are known whose calculated mean density is very much greater than that of any terrestrial matter. The classical example is the companion of Sirius. The mass of this star, as determined from the double-star orbit, is about ·85 that of the sun. It is a white star, its spectral type (A7) corresponding to an effective surface temperature of about 8000°. The luminosity, however, is very small, the absolute magnitude being 11·3. From the effective temperature and the absolute magnitude the radius can be calculated, and hence the mean density obtained. It is found to be about 50,000 gm./c.c. Stars of this type are classed as "white dwarfs," and although few are known with certainty, there is little doubt that they may be common objects in space, for, unless they were fairly near the sun, they would escape observation.

At the temperatures in the interior of stars atoms will be highly ionized, and if in white dwarfs the last stages of the process are reached, the atoms being broken up into nuclei

* Communicated by Prof. R. Whiddington, D.Sc., F.R.S.

and free electrons, there is no immediate difficulty in the existence of high densities. On a naïve view as to the "sizes" of electrons and nuclei (with radii some 10^{-5} times that of atoms) densities of the order of 10^{14} or 10^{15} would not be impossible.

Eddington * pointed out that on the usual classical theory a condensed star of the white dwarf type would not have sufficient energy to "cool down" to the ordinary uncondensed condition with unionized atoms. This paradox was cleared up by Fowler †, who applied the Fermi-Dirac statistics to matter at high densities. He found that the ultimate state was one in which the star was analogous to a gigantic molecule with only one configuration possible, and so effectively with temperature zero, and with no capacity for radiating, but none the less with a high energy.

In this paper a further application of the Fermi statistics will be made. The purpose is to discuss, under simplifying assumptions, whether there may be a limiting density due to the "jamming" of the electrons (owing to the exclusion principle which forms the basis of the Fermi statistics) independently of effects due to the appreciable size of any remaining incompletely ionized atoms.

Jeans ‡ has put forward a remarkable and beautiful theory to account for the distribution of stars in the Russell temperature-luminosity diagram. Roughly, the tenanted portions of the diagram are supposed to correspond to stable states which are only possible when there are departures from the ideal gas laws in the stellar interiors; these behave as if in a "quasi-liquid" condition owing to the congestion of the atoms. The general idea may be indicated by a consideration of the process of shrinkage of a star associated with the radiation of energy and increase in temperature. Suppose the atoms to be ionized as far as the M-ring, leaving the K- and L-rings intact. The star will be unstable until the shrinkage has continued so far that there is a certain amount of "jamming" of the atoms (L-ring congestion). This will eventually be relieved by ionization due to increase of temperature, when another unstable state will set in, to be succeeded by the K-ring congestion state. Ionization of the K ring will lead to the white dwarf stage.

* A. S. Eddington, 'The Internal Constitution of the Stars,' p. 172 (Cambridge Univ. Press, 1926).

† R. H. Fowler, "On Dense Matter," Monthly Notices of the R. A. S. lxxxvii. p. 114 (1926).

‡ J. H. Jeans, 'Astronomy and Cosmogony,' ch. v. (Cambridge Univ. Press, 1928).

About the last stage, Jeans says * : "In the white dwarfs the atoms are mainly ionized down to their nuclei, but a few K-ring atoms remain, and these, although few in number, probably occupy the major part of the available space; it is their jamming, rather than that of the nuclei, which results in the departures from the gas laws which ensure the stability of the star." It is in this connexion that there is considerable interest in the question as to whether there is a limit to electron "congestion" (using the word in the sophisticated sense already indicated) under the gravitational conditions in stars.

Approximate Calculation of Limiting Density.

The case of a sphere of uniform density of material composed of completely ionized atoms will be considered; the density increases as the sphere shrinks, and the limit will be reached when the gravitational energy released just supplies the energy required to squeeze the electrons closer together. The limiting case of high density occurs when the effective temperature is zero. (Compression necessitates addition of energy, for, since the phase-space is unchanged, and the volume is decreased, the limits of the momentum-space must be increased; in other words, the mean kinetic energy of the electrons must be increased.) The essential feature of the Fermi statistics applied to an assembly of free electrons is that not more than two electrons can occupy the same cell (of 6-volume h^3) in 6-dimensional phase-space. In the limit considered the cells occupied will be those corresponding to the lowest energies, and the mean kinetic energy per electron is then given by †

$$\frac{3}{40}\left(\frac{3}{\pi}\right)^{2/3}\frac{h^2n^{2/3}}{m},$$

where n is the number of electrons per unit volume. (This expression differs from that originally given by Fermi for *atoms*, being smaller by a factor $2^{2/3}$, necessitated by the statistical weight of the electron being 2, corresponding to its two orientations in a magnetic field.)

In fully ionized material the mean molecular weight is approximately equal to $2{\cdot}5\,m_{\mathrm{H}}$ (m_{H} = mass of hydrogen atom) ‡. Let M be the mass of a sphere of radius r of uniform density.

$$\mathrm{M} = \tfrac{4}{3}\pi r^3(2{\cdot}5\,m_{\mathrm{H}}n).$$

* *L. c.* p. 156.

† See, for example, G. Birtwistle, 'The New Quantum Mechanics,' p. 243 (Cambridge Univ. Press, 1928).

‡ Jeans, *l. c.* p. 75.

Let N be the total number of "molecules" in the mass.

$$N = \tfrac{4}{3}\pi r^3 n = \frac{M}{2{\cdot}5\, m_H}.$$

The number of "molecules" is very nearly equal to the number of free electrons, and since the kinetic energy of the nuclei will be relatively small, the total kinetic energy E_K, to a close approximation, is given by

$$E_K = \frac{3}{40}\left(\frac{3}{\pi}\right)^{2/3} \frac{h^2 n^{2/3}}{m} \cdot \frac{M}{2{\cdot}5\, m_H}.$$

The gravitational energy E_G is given by *

$$E_G = -aG\frac{M^2}{r},$$

where G is the gravitational constant, and $a = \frac{3}{5-n}$. The value of n depends on the distribution of density. For uniform density, the case here considered, $n=0$, so that $a = \frac{3}{5}$.

$$E_G = -\frac{3}{5} G \frac{M^2}{r} = -\frac{3}{5} \frac{GM^2(\frac{4}{3}\pi n)^{1/3}(2{\cdot}5\, m_H)^{1/3}}{M^{1/3}},$$

substituting the value of r in terms of M, n, and m_H.

The star will be able to contract, the released gravitational energy increasing the star's temperature until the energy given up is no longer sufficient to maintain the star at temperature zero; decrease in the volume occupied by the electrons necessitates an increase in their average momentum, and if the gravitational energy is insufficient for this, further contraction will be impossible. (The change in the negative electrostatic potential energy is neglected, as this for large densities will be small compared with the change in kinetic energy, as shown by an argument of Fowler †.) The condition for limiting density is given by

$$\frac{d}{dn}(E_K + E_G) = 0.$$

Writing

$$E_G = -\alpha n^{1/3}, \quad \text{where } \alpha = \frac{3}{5} GM^{5/3}(\tfrac{4}{3}\pi \times 2{\cdot}5\, m_H)^{1/3},$$

$$E_K = \beta n^{2/3}, \quad \text{where } \beta = \frac{3}{40}\left(\frac{3}{\pi}\right)^{2/3} \frac{h^2}{m} \frac{M}{2{\cdot}5\, m_H},$$

* Eddington, *l. c.* p. 87. † Fowler, *l. c.* p. 119.

n is a maximum when

$$\tfrac{1}{3}\alpha n^{-2/3} = \tfrac{2}{3}\beta n^{-1/3},$$

$$n = \left(\frac{\alpha}{2\beta}\right)^3.$$

Substituting the values of α and β,

$$n = 10^4\left(\frac{\pi}{3}\right)^3 \frac{G^3 M^2 m_H{}^4 m^3}{h^6}.$$

Using the following values for the constants :—

$$G = 6{\cdot}66 \times 10^{-8}, \quad m_H = 1{\cdot}662 \times 10^{-24},$$
$$m = 9{\cdot}01 \times 10^{-28}, \quad h = 6{\cdot}55 \times 10^{-27},$$

this gives

$$n = 2{\cdot}31 \times 10^{-37}\, M^2,$$

or, expressing the mass as a fraction of that of the sun, M_s($M_s = 2{\cdot}0 \times 10^{33}$),

$$n = 9{\cdot}24 \times 10^{29}\left(\frac{M}{M_s}\right)^2.$$

For the maximum density,

$$\rho = 2{\cdot}5\, m_H n$$
$$= 3{\cdot}85 \times 10^6\left(\frac{M}{M_s}\right)^2.$$

Discussion.

For the two white dwarfs for which most data are available, the following figures are quoted from Jeans :—

	M/M_s.	Spectrum.	T_e.	E.	r/r_s.	$\bar{\rho}$.
Sirius B.....	·85	A7	8,000	·007	·03	50,000
O_2 Eridani B.....	·44	A0	11,200	·002	·018	98,000

T_e is the effective surface temperature, deduced from the spectrum ; E the amount of energy radiated in ergs per gram, deduced from the total radiation (obtained from the absolute magnitude) and the mass ; r, the radius (given as a fraction of that of the sun r_s), can be found from T_e and the absolute magnitude. (For Sirius B, M/r has been found from the Einstein shift of spectral lines.) From r and M the mean density $\bar{\rho}$ may be calculated. Among other dense stars may be mentioned van Maanen's star ($\bar{\rho} > 100{,}000$,

$E=\cdot001$, $r/r_s=\cdot009$) and Procyon B (ρ is probaby some tens of thousands, $E=\cdot0005$, $M/M_s=\cdot37$).

The mean densities will be much smaller than the central densities. If the gas laws were obeyed, for example, Eddington calculates * that the central density, ρ_c, of Sirius B would be about 3,000,000.

For uniform spheres of fully ionized matter of masses equal to those of Sirius B and O_2 Eridani, the calculation above yields the following values for the maximum limiting densities:—

For Sirius B.....	$M/M_s=\cdot85$,	$\rho_{max.}=2\cdot77\times10^6$.
For O_2 Eridani B...	$M/M_s=\cdot44$,	$\rho_{max.}=7\cdot48\times10^5$.

These values are of the same order of magnitude as those calculated for the central densities. Actually the stars are not at absolute zero, or they would not radiate at all, but the calculation remains approximately valid up to temperatures of the order of some million degrees, because the assembly of free electrons at these high concentrations will remain an almost completely degenerate system. (Sommerfeld's degeneracy criterion †, $\frac{nh^3}{2}\frac{1}{(2\pi mk\mathrm{T})^{3/2}}>1$, gives with $n=10^{30}$, $\mathrm{T}<3\cdot5\times10^9$; with $n=10^{27}$, $\mathrm{T}<3\cdot5\times10^7$.) These considerations suggest that in white dwarfs there is a central portion in which most of the mass is concentrated, and whose density approaches the limiting value; and that this central portion is surrounded by a more diffuse layer, the condensed state gradually changing into the ordinary ionized gas state as the edge of the star is approached.

The radius ($r_{min.}$) of a completely condensed star of mass M may be readily obtained:

$$\tfrac{4}{3}\pi r_{min.}^3\rho_{max.}=\mathrm{M}.$$

Writing r_s, M_s, and ρ_s for the radius, mass, and mean density of the sun ($\rho_s=1\cdot42$),

$$\left(\frac{r_{min.}}{r_s}\right)^3=\frac{\mathrm{M}}{M_s}\frac{\rho_s}{\rho_{max.}}.$$

This gives, as the values of $\frac{r_{min.}}{r_s}$ for Sirius B, $\cdot0075$, and for O_2 Eridani B $\cdot011$, as compared with the values of $\frac{r}{r_s}$ of $\cdot03$ and $\cdot018$. It would appear that O_2 Eridani B has

* Eddington, *l. c.* p. 174.

† A. Sommerfeld, *Zeits. f. Phys.* xlvii. p. 1 (1928).

much more nearly approached the completely condensed condition, which is in keeping with its smaller radiation per gram than that of Sirius B (·002 as compared with ·007 erg).

On this view the central portion would be in a practically incompressible state, and so would be in the "quasi-liquid" condition which Jeans postulates as essential to the stability of stars. The essential point is that such a condition of congestion can be brought about solely on account of the "space requirements" of the electrons, and that it is not necessary to assume that there is any "jamming" of a few remaining K-ring atoms.

Similar phase-space considerations, however, do nothing to clear up the difficulties in Jeans's theory in connexion with more ordinary stars. In order that there should be the necessary deviations from Boyle's law in matter at the densities and temperatures deduced for the central regions, the effective volumes of the atoms (ionized down to the K, L, M ... rings, according to the conditions), must be much greater than that suggested by the orbital theory of the atom*. The space-charge distribution model of the atom does not greatly change the estimates of atomic "sizes," as is seen by an inspection of the curves given by Hartree† for Rb^+. If, following Thomas‡, the phase-space method is used for obtaining a rough estimate of the volume occupied by electrons in atoms, values of the same order of magnitude are obtained.

For Jeans's liquid-star theory it is not only necessary that the sizes of incompletely ionized atoms should be much greater than those estimated, but also that the volume "required" by an atom with, say, all its L-electrons just before the temperature is great enough to ionize the L-ring should be much larger th n the volume required by the L-ionized atom, together with the free L-electrons, after ionization. Phase-space consideration suggests that there should be little change in the required volume.

The fact that there are these difficulties does not, of course, necessarily invalidate Jeans's general explanation of the non-uniformity of distribution of stars in the temperature-luminosity diagram. Rather its inner coherence is so striking as to suggest that there are other unknown or unrecognized factors to be considered on the atomic theory side.

* Jeans, *l. c.* p. 159.
† D. R. Hartree, Proc. Camb. Phil. Soc. xxiv. p. 111 (1928).
‡ L. H. Thomas, Proc. Camb. Phil. Soc. xxiii. p. 542 (1927).

Summary.

Using the Fermi statistics, it is shown that, under the influence of gravitational and electron "packing" effects, the limiting density ρ of a uniform sphere of mass M, consisting of a mixture of fully-ionized atoms, is approximately given by

$$\rho = 3{\cdot}85 \times 10^6 \left(\frac{M}{M_s}\right)^2,$$

where M_s is the mass of the sun.

For spheres with the masses of Sirius B and O_2 Eridani B the limiting densities are $2{\cdot}8 \times 10^6$ and $7{\cdot}5 \times 10^5$.

It is suggested that white dwarfs contain a core of material approaching the limiting density, the ratios of the radius of the core to the radius of the star, in the two cases considered, being about ·25 and ·61. The core will be in an almost incompressible or "quasi-liquid" state, due to the "congestion" of the electrons.

Jeans's theory of the distribution of stars in the Russell temperature-luminosity diagram is briefly discussed. It is shown that the quasi-liquid state required for stability may be attained in white dwarfs owing simply to electron-packing, without the necessity of assuming "jamming" of the few remaing K-ring atoms.

Physics Department,
The University, Leeds.
October 1928.

VI. *Radiometer Effect of Positive Ions.* *By* Chas. T. Knipp, *Ph.D., Professor of Experimental Electricity, University of Illinois, and* Wesley S. Stein, *M.A.**

I. *Introduction.*

THE rolling of a Crookes mica mill-wheel in a vacuum by a beam of cathode rays is a well-known phenomenon. As to the nature of the force exerted, J. J. Thomson †, after calculating the possible force due to change of momentum of the particles upon impact, concluded that the "movement is probably due to an effect similar to that observed in a radiometer, as the impact on the vanes will make one side of

* Communicated by the Authors.

† J. J. Thomson, Cond. Elec. through Gases, 2nd ed. p. 630.

the vanes hotter than the other." Starke * showed this to be the case by using the apparatus in which the radiometer effect was eliminated. He suspended a flat disk by a fine wire fastened at the centre of the disk. A beam of cathode rays was directed against the bottom of the disk near its outer edge and at an angle of 45° with the vertical and with the tangent to the disk at the point of incidence. The arrangement, being comparatively insensitive to vertical forces, was not affected by the radiometer effect nor by the vertical component of the direct mechanical force. The horizontal component should produce a rotation. Starke found no sensible deflexion, thus proving that the direct mechanical effect, due to a beam of cathode rays, was below the sensitivity of his instrument, which was 10^{-4} dyne.

The corresponding phenomenon in the case of positive rays is not so well known, and no conclusive data seem to have been taken to show whether the force exerted by a beam of positive rays is a secondary effect, as in the case of cathode rays, or whether the force is purely mechanical.

Swinton † observed the rotation of wheels having mica and aluminium vanes, respectively, when placed in the path of positive rays. In the case of mica vanes he measured the difference in temperature between the sides of the vane. The maximum temperature difference observed was 200° centigrade. He also observed that the greatest speed of rotation took place when the difference in temperature was the greatest, and hence concluded that the effect was a secondary or radiometer effect.

The purpose of the present investigation has been to study still further the nature of the force exerted by a positive ray beam, and to arrive, if possible, at a more satisfactory explanation of the phenomenon.

II. *Theory.*

If we know the kind of ions which compose the beam; and also their velocity and the number striking the vane per second, it is possible to predict the direct mechanical force due to the beam when the ions lose all their momentum upon striking the vane. In the present experiment the gas in the tube was residual air, and it is also known that under the conditions of this experiment most of the positive ions are atomic in size and singly charged. Also, the error introduced into the calculated value of the force by the

* Starke, *Ann. d. Phys.* iii. p. 101 (1900).
† Swinton, Proc. Roy. Soc. lxxix. p. 391 (1907).

presence of some molecular ions will tend to cancel that introduced by the presence of a number of doubly-charged ions in the beam. We may then assume singly-charged atomic ions. There are usually a few negatively-charged ions in the positive-ray beam, the presence of which would make the calculated value of the force a little too low. This error helps to counteract the error due to the fact that not all the positive ions have a velocity as great as that corresponding to the total potential drop across the tube, which is the only value available for use in the calculations. The error due to the use of the total potential drop in the calculations is probably the only one which might be large enough to seriously affect the validity of the result.

Keeping in mind the foregoing conditions, we may write

$$1/2mv^2 = \mathrm{V}e,$$

where m is the mean atomic weight for air and was taken to be 14·4. All quantities are measured in electromagnetic units. Then

$$v = \sqrt{\frac{2\mathrm{V}e}{m}}.$$

The momentum of a single ion travelling with the velocity v is accordingly

$$mv = \sqrt{2\mathrm{V}em}.$$

When an ion is stopped by the vane, assuming it is not reflected, the change of momentum will also be

$$\sqrt{2\mathrm{V}em}.$$

But from Newton's second law

$$\mathrm{F} = \frac{d}{dt}(mv).$$

In this case the rate of change of momentum is equal to n (the number of ions striking the vane per second), multiplied by the momentum which each ion loses upon impact. Hence

$$\mathrm{F} = n\sqrt{2\mathrm{V}em}.$$

But

$$n = \frac{i}{e};$$

therefore F may be written

$$\mathrm{F} = i\sqrt{\frac{2\mathrm{V}m}{e}}.$$

If i is measured by a galvanometer and V by a calibrated spark-gap, the value of F is known. This formula applies

only when the direction of the beam and the direction of motion of the vane coincide. When the angle between the two directions is θ the value above must be multiplied by $\cos\theta$. The general formula is then

$$F_{obs.} = i\sqrt{\frac{2V\overline{m}}{e}}.\cos\theta.$$

To calculate the actual force of the beam from measurements of the twist in the suspension, it is necessary to find the amount of force applied to the vane which is required to cause a twist of the suspension through one radian. Using the formula for the torsion pendulum,

$$T = 2\pi\sqrt{\frac{I}{c}},$$

we have an expression for c, the constant of torsion, in terms of T the period and I the moment of inertia. To find T and I a piece of aluminium, of weight comparable to the weight suspended while in use and of such shape that its moment of inertia could easily be calculated, was suspended and the period of the pendulum found. Hence

$$c = \frac{4\pi^2 I}{T^2},$$

where T and I are known. To find F it is merely necessary to divide by the length of the lever-arm. Hence

$$F_{calc.} = \frac{c}{d} = \frac{4\pi^2 I}{T^2 d}.$$

This is the force which has to be applied to the vane to twist the suspension through one radian. The twist being measured, the total force can be found.

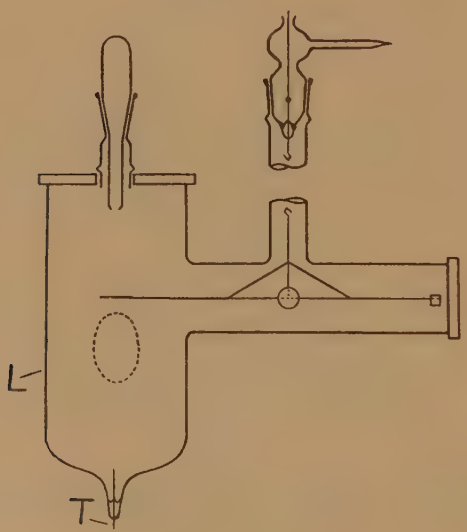
III. *Apparatus.*

The first type of apparatus used in this investigation was basically a Knipp-Kunz * positive-ray tube having a shutter in front of the positive-ray orifice and a side-tube allowing a thin aluminium vane to be inserted across the path of the positive-ray beam. The cathode was a hollow aluminium cylinder 2·5 cm. in diameter and 5 cm. long, completely closed except for a 3-mm. hole at the centre of each end. The shutter was mounted upon a brass rod pivoted upon a tungsten point, and could thus be grounded. The shutter itself was made of two parts. One was of thin microscope

* Knipp, Trans. Ill. Acad. Sci. x. p. 283 (1918).

cover-glass, which cut off the rays but permitted light from the discharge to pass through and fall upon the vane. The other part was of thin aluminium, which cut off both the ions and the light. A fine silver suspension was used at first, but this was found to be too delicate. It was replaced by a phosphor-bronze strip. Its length was 25 centimetres. The vane was a thin sheet of aluminium 2 cm. square, mounted vertically upon one end of an aluminium cross-bar. The apparatus was so designed that the cross-bar and vane could be inserted into the side-tube and hooked to the

Fig. 1.

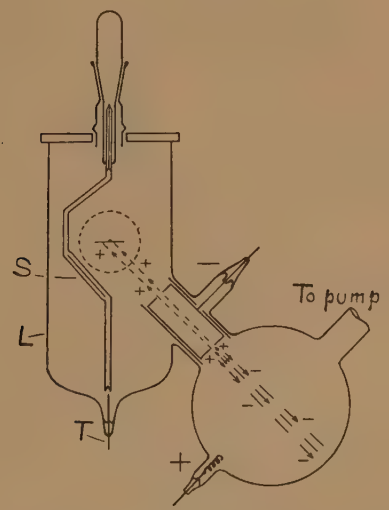


suspension by a hook at the back of the mirror. The inside of the tube containing the cross-bar as well as that part of the discharge-tube containing the vane were lined with aluminium foil in order to shield the suspended system from electrostatic effects. The shielding metal and shutter were grounded.

The type of apparatus described above is suitable for measuring the force caused by a positive-ray beam, but does not discriminate between direct mechanical force and a secondary radiometer effect. Hence the apparatus shown in figs. 1 and 2 was finally constructed. It operates on the same principle as that used by Starke referred to earlier in

this paper. It differs from the first apparatus mainly in that the vane is mounted in an horizontal position and that the rays strike it from below at an angle (fig. 2) of 45°. The shutter S is shown swung out of line of the positive-ray beam. To overcome any dissymmetry of the beam, the cathode was enclosed in a separate glass collar (also shown in fig. 2) which extended far enough to protect the beam from the effects of the unsymmetrical location of the glass caused by the 45° junction. The tubes containing the cross-bar and suspension were made larger than in the first apparatus in order to facilitate the insertion of the sus-

Fig. 2.



pended system. The chamber L was closed at the top by a glass plate, a feature which made the insertion of the shutter and shielding easy. These were grounded through T. This apparatus was constructed of Pyrex glass beakers and Florence flasks.

A sensitive galvanometer was used to measure the current to the vane, and the potential across the tube was measured by a sphere-gap. At first centimetre spheres were used, but these were replaced by a calibrated sphere-gap between spheres 12·5 cm. in diameter. This gap, which was made by the Victor X-ray Supply Company of Chicago, has a screw adjustment and scale which made possible quite accurate readings.

IV. *Observations.*

The electric wiring connected the shutter and shielding to ground, and also connected the suspended system to ground through the galvanometer. With the first apparatus the cross-bar was centred as nearly as possible along the axis of the tube and let come to rest. Then, with the aluminium shutter interposed, the discharge was started and the cross-bar observed. It was found that the only movement which occurred was a slight irregular shifting, the direction of which depended upon the direction the cross-bar happened to be off centre at the time the discharge was started. This procedure was then repeated with the glass shutter and the same results obtained. These trials were repeated at various times, always with similar results. Hence the effect due to the light from the discharge was less than 10^{-4} dyne.

In making observations of the force exerted by the beam, the equilibrium position was noted with the discharge running and the shutter closed. The shutter was then opened and the torsion head rotated sufficiently to bring the cross-bar back to the same position. The precaution of balancing the cross-bar with the shutter closed and the discharge running was for the purpose of eliminating the effect of the spurious drift described above, which seemed to depend upon the position of the balance. The number of degrees of rotation necessary to bring back the cross-bar was read off on a scale fastened at the torsion head. The pressure, galvanometer deflexion, and potential drop across the tube were also recorded. Since it was impossible to take all readings simultaneously, it was necessary to make observations only when the conditions remained fairly constant. It was found necessary to use a weak magnetic field to deflect all electrons from the beam in order to get the true value of the positive current.

Typical data obtained with the first apparatus by the procedure outlined above are included in Tables I. and II.

The procedure in making observations with the second tube was similar to that used with the first. However, since the deflexions of the vane were quite small in this case, it was found better not to turn the torsion head, since it was liable to set the vane swinging, but to read the deflexion directly from marks placed on the plate glass at the end of the cross-bar opposite the vane. In reading a position the observer always sighted along the end of the cross-bar and the vertical suspension. Because of the small size of the

TABLE I.

Galv. Deflex. (mm.).	Vane Deflex. (degrees).	Potential (volts).	Pressure (mm. Hg).
18·5	35	30,000	·00030
16·5	25	30,000	·00028
18·5	33	30,000	·00029
19·5	40	30,000	·00030
19·0	42	30,000	·00029
18·8	41	30,000	·00029
17·5	37	30,000	·00030

$F_{calc.} = ·0149$ dyne.

$F_{obs.} = ·0143$ dyne.

TABLE II.

Galv. Deflex. (mm.).	Vane Deflex. (degrees).	Potential (volts).	Pressure (mm. Hg).
25·0	21	30,000	·00034
31·0	46	30,000	·00030
29·0	44	30,000	·00028
34·0	40	30,000	·00028
28·5	34	30,000	·00029
33·0	34	30,000	·00029
32·5	34	30,000	·00027
36·5	36	30,000	·00029
36·5	35	30,000	·00024

$F_{calc.} = ·0145$ dyne.

$F_{obs.} = ·0140$ dyne.

TABLE III.

Galv. Deflex. (mm.).	Vane Deflex. (mm.).	Potential (volts).	Pressure (mm. Hg).
7·0	7·0	18,000	·00028
6·5	5·0	17,000	·00034
7·0	7·0	17,500	·00032
6·5	7·5	17,500	·00030
7·0	7·5	18,000	·00032
7·0	8·0	18,000	·00024
7·0	7·5	17,500	·00026
6·5	8·0	18,000	·00026

$F_{calc.} = ·0017$ dyne.

$F_{obs.} = ·0012$ dyne.

deflexions observed with the second type of apparatus, it was imperative that the needle should be allowed to become very quiet before an observation was made. Typical data obtained by the second method are given in Tables III. and IV.

The values for $F_{calc.}$ which are recorded in the above two tables were calculated in the same manner as in Tables I. and II., except that in the latter case θ was 45 degrees.

V. *Discussion of Results.*

Although the data obtained by the first method led to values of $F_{obs.}$ which agree very well with $F_{calc.}$, yet nothing is proven by the close agreement, since we do not know

Table IV.

Galv. Deflex. (mm.).	Vane Deflex. (mm.).	Potential (volts).	Pressure (mm. Hg).
14·5	10·0	12,000	·00132
13·5	6·0	12,000	·00108
15·0	9·0	10,000	·00090
16·0	6·0	13,000	·00082
17·5	6·0	12,500	·00082
18·0	6·0	13,000	·00078
19·0	8·0	13,000	·00078

$F_{calc.} = \cdot 0033$ dyne.

$F_{obs.} = \cdot 0013$ dyne.

what percentage of the force is due to a radiometer effect and what to direct mechanical effect; however, the results do suggest a probable slowing-down of the rays by the residual air in the tube. This, as may be seen by averaging the values in Tables I. and II., amounts for the particular pressure used to about 4 per cent.

The fact, however, that a measurable force was detected with the second apparatus is important, since it shows that, contrary to what was previously thought, at least a part of the bombardment of a beam of positive rays results in a direct mechanical effect. By referring to Table III., in which the radiometer effect is eliminated, it is seen that the observed values of F are about 29 per cent. lower than the calculated values; *i. e.*, the value of the direct mechanical effect, in this instance, is 71 per cent. of the value calculated on the theory given in section II. of this paper. These two values are not corrected for the slowing-down of the rays due

to the presence of residual air. This residual-air effect is the same in Table III. as it is in Tables I. and II., since the pressure was kept approximately constant. It is a question how to proportion this correction between the radiometer and mechanical effects. We have tentatively assumed it to be in the ratio of 1 : 4. Hence, taking the residual-air effect as 4 per cent., we may write radiometer effect 28 per cent., and mechanical effect 68 per cent. These data are shown under I. and II., also III., in Table V. Apparently the proportion between radiometer and mechanical effects depends also upon the material and thickness of the vane. In this case the vane was ·1 mm. thick and the pressure was ·0003 mm. of mercury.

A glance at Table IV. reveals the fact that pressure has a marked effect upon the results. With the pressure at

TABLE V.

Table	Radiometer and Mechanical Effect. (%).	Radiometer and Residual-Air Effect. (%).	Radiometer Effect. (%).	Residual-Air Effect. (%).	Mechanical Effect. %).	Total.
I. & II. (averaged).	*96*	?	?	*4*	?	100
III. ...	96	29	*28*	*4*	*68*	100
IV.....	67	60	*28*	*32*	*39*	99

·0009 mm. Hg the rays were slowed down sufficiently so that their actual force on the vane was only about 39 per cent. of the calculated value. Here, again, it is difficult to state the results definitely. Assuming that the radiometer effect is the same as in Table III. (which assumption is open to question), the distribution may be set down roughly as in IV. of Table V.

It is the intention of the writers to collect additional data over a considerable range of pressures with both the first and second types of apparatus in order to arrive more nearly at the exact magnitude of the various effects, and also how they vary. All calculations were made on the assumption that the positive ions are not reflected when they strike a grounded vane. This should also be tested experimentally.

Laboratory of Physics,
University of Illinois.
June 15, 1928.

VII. *The Dispersion of Double Refraction in Quartz.*

By F. C. Harris, *M.Sc., University College, London* *.

[Plate I.]

In connexion with some recent researches in photo-elasticity, a pair of left-handed quartz wedges, arranged as a parallel plate whose thickness could be varied by sliding one wedge over the other, were used to measure the retardation produced in bodies under pressure. It became necessary therefore to investigate the dispersion of double-refraction in the quartz for a much larger number of wave-lengths throughout the visible spectrum than had been done by previous investigators, and it was with this object that the research here described was carried out.

The two quartz wedges, placed together as a parallel plate, cut parallel to the optic axis, were mounted on the "prism table" of a spectroscope in such a way that they could be rotated as a whole plate about this optic axis.

Light from a Point-o-Lite lamp passed horizontally through the plate—*i. e.*, perpendicular to the optic axis. The plate was situated between crossed nicols, and an image of it was focussed by a lens on the slit of a Littrow spectrograph, as in fig. 1 (Pl. I.).

The image seen in the camera of the spectrograph consisted of a continuous spectrum crossed by a number of vertical black bands. By means of a small reflecting prism and a shutter, a comparison spectrum of the iron arc was obtained on either side of the "banded" spectrum, as in fig. 2 (Pl. I.).

The quartz plate was carefully adjusted so that the light passed normally through it, and a photograph of the bands and comparison spectrum was taken. This photograph was then carefully measured on a Hilger plate-measuring machine and the wave-length of the middle of each band determined.

To find the order of any particular band, the comparison spectrum was removed and replaced by a sodium flame, and also the camera was replaced by a telescope. By rotation of the plate about the optic axis, a band could be brought into coincidence with the sodium lines. The angles of rotation required to bring bands of successive orders into such coincidence with the sodium lines were determined, and from these observations the order n of the band nearest the

* Communicated by Prof. L. N. G. Filon, F.R.S.

sodium lines at normal incidence was calculated from the following well-known formula :—

$$\text{Time retardation} = \frac{t}{v_0}\{\mu_1 \cos r_1 - \cos i\} = \tau_1,$$

where t = thickness of plate,
v_0 = velocity of light in air,
i = angle of incidence,
r_1 = angle of refraction for the ordinary ray,
μ_1 = ordinary refractive index.

Now,

$$\mu_1 \cos r_1 = \sqrt{\mu_1^2 - \sin^2 i}.$$

$\therefore$ For the ordinary ray $\tau_1 = \frac{t}{v_0}\{\sqrt{\mu_1^2 - \sin^2 i} - \cos i\}$,

Similarly,

For the extraordinary ray $\tau_2 = \frac{t}{v_0}\{\sqrt{\mu_2^2 - \sin^2 i} - \cos i\}$.

$\therefore$ The time retardation between the ordinary and extraordinary rays due to a thickness t of the quartz

$$= \tau_2 - \tau_1 = \frac{t}{v_0}\{\sqrt{\mu_2^2 - \sin^2 i} - \sqrt{\mu_1^2 - \sin^2 i}\}.$$

The equivalent retardation in centimetres of air

$$= v_0\tau_2 - v_0\tau_1 = t\{\sqrt{\mu_2^2 - \sin^2 i} - \sqrt{\mu_1^2 - \sin^2 i}\}.$$

Now, if λ is the wave-length of any band of order n for normal incidence,

$$n\lambda = t(\mu_2 - \mu_1). \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

If a rotation i is now made which brings the band of order $(n+p)$ on to the same wave-length λ, we have

$$(n+p)\lambda = t\{\sqrt{\mu_2^2 - \sin^2 i} - \sqrt{\mu_1^2 - \sin^2 i}\}, \quad . \quad (2)$$

and from (1) and (2) we get

$$\frac{(n+p)\lambda}{n\lambda} = 1 + \frac{p}{n} = \frac{\sqrt{\mu_2^2 - \sin^2 i} - \sqrt{\mu_1^2 - \sin^2 i}}{\mu_2 - \mu_1}$$

$$= \frac{\mu_2^2 - \mu_1^2}{(\mu_2 - \mu_1)\{\sqrt{\mu_2^2 - \sin^2 i} + \sqrt{\mu_1^2 - \sin^2 i}\}}$$

$$= \frac{\mu_2 + \mu_1}{\sqrt{\mu_2^2 - \sin^2 i} + \sqrt{\mu_1^2 - \sin^2 i}}.$$

If successive bands are now brought into coincidence with the sodium lines as above, p has the values 1, 2, 3, ... etc.

Hence, substituting the measured values of i, and taking the values of μ_1 and μ_2 from those of Gifford * for the particular wave-length $\lambda=5893$, a series of approximate values of n is obtained.

But n is known to be an integer, and hence n can be determined exactly. Thus Gifford's value of $\mu_2-\mu_1$ is only used to give an indication of the order n, the actual results obtained being independent of his values.

The procedure is then as follows :—

Let the band nearest the sodium lines be of order n. Rotate the plate to bring this band into coincidence with the cross-wire of the telescope, which has previously been set on one of the sodium lines. Let the angle of rotation from the normal be i_1.

Then

$$n\lambda = t\{\sqrt{\mu_2^2-\sin^2 i_1}-\sqrt{\mu_1^2-\sin^2 i_1}\}.$$

Rotate further, so that the band of order $n+p$ is on the cross-wires. Let the angle of incidence be i_2.

Then

$$(n+p)\lambda = t\{\sqrt{\mu_2^2-\sin^2 i_2}-\sqrt{\mu_1^2-\sin^2 i_2}\}.$$

From these last two equations we have

$$1+\frac{p}{n}=\frac{\sqrt{\mu_2^2-\sin^2 i_2}-\sqrt{\mu_1^2-\sin^2 i_2}}{\sqrt{\mu_2^2-\sin^2 i_1}-\sqrt{\mu_1^2-\sin^2 i_1}}.$$

If $p=1$,

$$1+\frac{1}{n}=\frac{\sqrt{\mu_2^2-\sin^2 i_1}+\sqrt{\mu_1^2-\sin^2 i_1}}{\sqrt{\mu_2^2-\sin^2 i_2}+\sqrt{\mu_1^2-\sin^2 i_2}}.$$

Repeat measuring angles i_3, i_4, etc. ... for values of $p=2$, 3, 4, ... etc.

A series of values of n will thus be obtained from which the true value—*i. e.*, the integer—is determined.

For the particular plate used the values of n thus found were 77·36 ; 77·06 ; 77·08 ; 77·01 ; 77·11 ; 76·98 ; 76·80 ; 76·83 ; 76·93 ; 76·92. Obviously the integral value of n was 77.

Having determined n for one particular band, the orders of all the other bands in the spectrum are known.

* Gifford, Proc. Roy. Soc. A, lxx. p. 329 (1902), and lxxxiv. p. 193 (1910).

Now for any band at wave-length λ.

$$\text{Total retardation} = n\lambda = t \,.\, \phi(\lambda),$$

where $\phi(\lambda)$ is the value of $\mu_2 - \mu_1$ at wave-length λ.

$$\therefore \qquad \phi(\lambda) = \frac{n}{t} \,.\, \lambda.$$

By assuming the value of $\phi(\lambda)$ as obtained by previous investigators for one particular wave-length, the thickness of the plate t can be calculated, and hence the value of $\phi(\lambda)$ at any other wave-length λ can be determined.

The value of $\phi(\lambda)$ used here was taken from Gifford's values for $\lambda = 5899{\cdot}693$,—this being the wave-length of the band of order 76,—and this gave the thickness $t = 4{\cdot}92224$ mm. A measurement of t by a micrometer screw-gauge reading to $\frac{1}{1000}$ inch gave $t = 4{\cdot}94$ mm.

Hence, t being known, the values of $\phi(\lambda)$ for these wave-lengths corresponding to successive bands throughout the spectrum, as measured from the photograph, could now be calculated. This was done for 57 bands, the results being given in the following table :—

Table of Values of $\phi(\lambda) = \mu_2 - \mu_1$ for Quartz.

Wave-length λ.	$\phi(\lambda) = \mu_2 - \mu_1$.	Wave-length λ.	$\phi(\lambda) = \mu_2 - \mu_1$.
7116·052	0·008963	(6438	0·009044)
(7066	0·008987)	{6437	0·00897}
7011·389	0·008974	6365·149	0·009052
6910·607	0·008985	6282·488	0·009062
6813·913	0·008998	6200·737	0·009070
6719·078	0·009009	6122·355	0·009080
(6708	0·009013)	[6076	0·009077]
6626·274	0·009019	6047·303	0·009091
(6563	0·009017)	5971·898	0·009099
6536·735	0·009030	*5899·693	0·009109
6448·948	0·009040	(5893	0·009110)

Observations due to other investigators :—

( ) Gifford, Proc. Roy. Soc. A, lxx. p. 329 (1902), and lxxxiv. p. 193 (1910).

{ } Sarasin, 'Smithsonian Tables,' table 193.

[ ] Ehringhaus, *Neues Jahrbuch d. Mineralogie*, xli. p. 342 (1916).

Table of Values of $\phi(\lambda)=\mu_2-\mu_1$ for Quartz (*cont.*).

Wave-length λ.	$\phi(\lambda)=\mu_2-\mu_1$.	Wave-length λ.	$\phi(\lambda)=\mu_2-\mu_1$.
{5892	0·00916}	4775·735	0·009314
5829·057	0·009119	4732·166	0·009325
5760·898	0·009129	4689·460	0·009337
5693·799	0·009138	{4676	0·00934}
5628·602	0·009148	4647·716	0·009348
(5607	0·009144)	4606·722	0·009359
5565·090	0·009158	4566·303	0·009370
5502·912	0·009167	4527·330	0·009382
(5461	0·009171)	4488·601	0·009393
5441·799	0·009176	4450·784	0·009404
5383·916	0·009188	[4415	0·009403]
{5377	0·00918}	{4414	0·00952}
{5336	0·00920}	4413·691	0·009415
5326·492	0·009198	4377·600	0·009427
5270·296	0·009208	(4359	0·009430)
(5270	0·009211)	4341·844	0·009438
5216·043	0·009219	(4341	0·009430)
5162·573	0·009230	4307·265	0·009451
5110·306	0·009240	4272·822	0·009462
[5097	0·009235]	4239·575	0·009474
{5084	0·00924}	4206·520	0·009486
5059·233	0·009250	4174·244	0·009498
5009·171	0·009261	4142·426	0·009510
4960·026	0·009271	4111·544	0·009522
4912·644	0·009282	4080·534	0·009533
4866·063	0·009293	[4054	0·009536]
(4861	0·009288)	4050·927	0·009547
4820·469	0·009304	(4046	0·009560)
(4800	0·009317)	4021·096	0·009558
{4799	0·00929}	3992·265	0·009571

Observations due to other investigators:—

( ) Gifford, Proc. Roy. Soc. A, lxx. p. 329 (1902), and lxxxiv. p. 193 (1910).

{ } Sarasin, 'Smithsonian Tables,' table 193.

[ ] Ehringhaus, *Neues Jahrbuch d. Mineralogie*, xli. p. 342 (1916).

Comparing the results of $\phi(\lambda)=\mu_2-\mu_1$, obtained by the present method, with those of previous investigators, it will be seen that :—

(a) *Gifford.* Present values agree within the limits of experimental error, throughout the whole table, with the exception of the extreme values, and even here the disagreement is not appreciable.

(b) *Sarasin.* In general, the agreement is very poor throughout, and at $\lambda=6437$, 5892, and 4414, the difference between the two sets is far greater than could possibly be accounted for by experimental errors.

(c) *Ehringhaus.* The present values are all slightly greater than these, but the difference between the two sets is practically constant throughout.

The agreement with Gifford is not surprising since the present determinations have been adjusted, as explained above, to give the same value at the particular wave-length $\lambda=5899{\cdot}693$. The discrepancies between the values now obtained and those of Sarasin are also to be expected, for the values of μ_2 and μ_1 given by Gifford and Sarasin respectively, differ appreciably, whereas there is fairly good agreement between the values given by Gifford and Ehringhaus.

The almost complete agreement between the present values and those of Gifford and Sarasin indicate that the law of dispersion of double refraction is sensibly identical in different specimens of quartz.

In conclusion, I should like to record my very sincere thanks to Prof. L. N. G. Filon, F.R.S., for his great help and encouragement throughout the progress of this research.

[*Note.*—A further measurement of the thickness t, by weighing the plate first in distilled water and then in air, correcting for pressure and temperature, gave the value 4·9124 mm.]

VIII. *The Action of Ionizing Radiations on Colloids.* By J. A. Crowther, *M.A., Sc.D., F.Inst.P., Professor of Physics in the University of Reading* *.

§1. *Preliminary.*

IT has been shown, in previous communications from this laboratory [1, 2, 3], that positively-charged colloids are affected by exposure to X-radiation. Lyophobic sols, such as a Bredig solution of copper, are precipitated by the radiation; lyophilic sols, such as ceric hydroxide, show first a rapid decrease in viscosity followed by a rise in viscosity with ultimate setting to a gel. We have suggested as a cause for these phenomena the gradual discharge of the charged colloidal particles by the ionization produced in the solution by the passage of the rays.

On this hypothesis it is to be expected that other ionizing agents, such as the beta-rays from radium, would produce similar results. Such an effect had, in fact, been already demonstrated for one or two lyophilic sols, in particular by Hardy [4] for positively-charged globulin solutions, and by Fernau and Pauli [5] for the ceric hydroxide sol. These experiments were qualitative rather than quantitative, and it was thought that a direct quantitative comparison between the effects of the two types of radiation would not be without interest. If the observed effects were due to the production of ions in the sol, they should depend only on the number of ions produced, and not upon the agent used for producing the ions. They would thus provide an additional test of this hypothesis.

The sols selected for the experiment were (*a*) a ceric hydroxide sol, (*b*) a Bredig solution of copper. The methods adopted for preparing these sols and investigating their behaviour under X-rays have been sufficiently described in previous communications, and were followed out without change in the experiments now to be described. Certain modifications in the procedure had to be made when exposing the sols to the beta-rays, as the intensity of the radiation, even from a strong radium source, is small in comparison with the output of an X-ray tube, and it was undesirable to prolong the time of exposure unduly.

The source of beta-radiation was a small thin-walled glass bulb, 0·95 cm. in diameter, containing initially rather more

* Communicated by the Author.

than 100 millicurie of radium emanation, which was very kindly supplied for the experiment by Prof. S. Russ, and the first operation was to measure the ionization produced by the beta-rays from this source in the ionization chamber employed in all our experiments for the measurement of the X-radiation. As it was undesirable to move either the X-ray tube or the ionization chamber, the emanation tube was clamped immediately in front of the window of the X-ray tube, it having been ascertained that at this distance the beta-rays would pass through the ionization chamber without falling directly on either of the electrodes. The ionization current in the chamber was then measured, using a Wilson electroscope and a suitable known capacity (0·0051 mf.). The aperture of the ionization chamber was then closed with a sheet of lead, and the ionization current, due now to the gamma-radiation only, was again measured. The difference between the two currents measured the ionization due to the beta-rays alone. The distance of the emanation bulb from the window of the ionization chamber was then measured, and the bulb removed.

We can now calculate the total charge which would pass across the ionization chamber during an exposure of, say, one hour, at a definite time, and at a definite standard distance, which in the actual experiment was 8·3 cm. It was found that the beta-ray current under these circumstances was 0·091 microcoulomb per hour. Since the emanation decays exponentially with the time, it is a simple matter to calculate the charge for an exposure of one hour at any later date, or, perhaps more simply, to calculate what length of exposure at the time when the ionization measurements were made is equivalent to an exposure of one hour at some later date. The times of exposure in this paper are all given in terms of this standard.

§2. *Experiments with Ceric Hydroxide Sol.*

The sol used in the experiments was of the type denoted by S/4 in the previous paper[2]. As the exposures to X-rays followed exactly the procedure described in detail in that communication, it is unnecessary to describe them further here. The viscosity of the sol after exposure to a measured dose of X-rays was compared with the viscosity of a second sample of the same sol which had been treated in exactly the same manner as the first except for the exposure to the rays. The percentage change in viscosity produced by the exposure is thus measured and plotted

against the dose, as measured by the total charge in micro-coulombs (mc.) which passed through the ionization chamber during the exposure. The results, as might be expected, showed exactly the same general features as those described in the earlier work. It was, however, necessary to make the observations afresh, as the numerical values vary with the age of the sol.

The exposures to beta-radiation were made with the same stock of sol, and were carried on simultaneously with the X-ray measurements. The method of exposure was, however, different. A small volume (1 c.c.) of the sol was placed in a rather large quartz test-tube with a hemispherical end. The bulb containing the emanation was supported centrally in the tube, so that exactly half the bulb was immersed in the sol, which then just filled the hemispherical end of the quartz tube. The tube was securely sealed during the exposure. The times of exposure varied from about twenty minutes up to three hours. The percentage change in viscosity was determined at the end of the exposure in exactly the same way as in the X-ray experiments.

The results of these two sets of experiments are given in Table I. The durations of the beta-ray exposures have been

TABLE I.

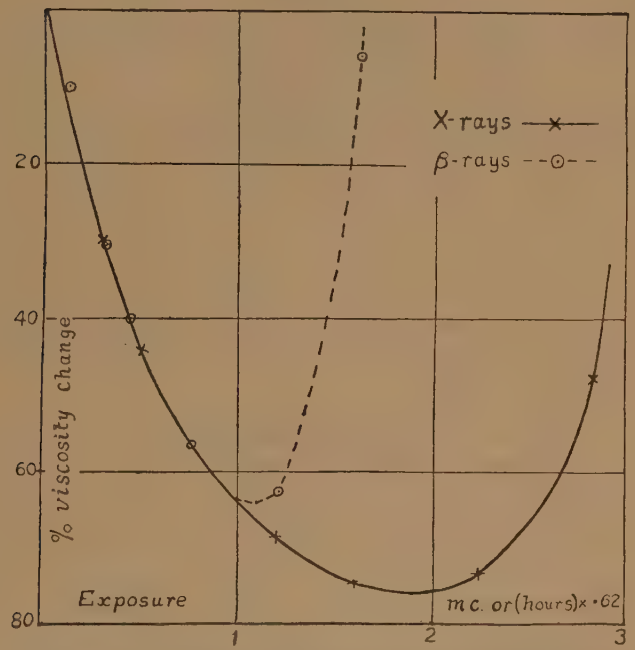
Effect of X- and β-rays on the Viscosity of a Cerium Sol.

X-radiation.		β-radiation.	
Dose in mc.	Per cent. decrease in viscosity.	Exposure in hours.	Per cent. decrease in viscosity.
·30	30·0	·25	7·3
·50	44·5	·50	30·6
1·20	68·5	·74	40·0
1·60	74·5	1·22	56·8
2·24	73·9	1·95	62·2
2·84	48·1	2·60	5·8

reduced to standard time, as previously explained. They are shown graphically in fig. 1, where the full curve with the crosses represents the X-ray results, and the broken curve and circles the beta-ray measurements. From these curves we can draw up a table comparing the amounts of X-ray exposure (in mc.) and beta-ray exposure (in hours) required to produce the same percentage change in the

viscosity of the sol. The figures are given in Table II It will be seen from the last column of this table that these exposures bear a ratio to one another which is constant up to a change in viscosity of 60 per cent. Thus, if we reduce

Fig. 1.



Changes in viscosities of ceric hydroxide sol with varying exposures to X- and β-rays.

TABLE II.

Equivalent X- and β-ray Exposures for a Cerium Sol.

Per cent. change in viscosity.	X-ray dose in m.c.	β-ray dose in hours.	hours. / mc.
−20	0·18	0·31	·58
−30	0·30	0·48	·62
−40	0·43	0·70	·61
−50	0·62	1·00	·62
−60	0·86	1·38	·62

the abscissæ of the dotted curve in the ratio of 0·62 to 1, the first portion of the beta-ray curve will lie almost exactly on that for X-rays. This is shown by the circles on this curve.

If we follow Smoluchowski and assume that the increased viscosity of a viscous solution is due to the charges carried by the colloidal particles, it follows that the first portion of the viscosity-dosage curves represent the gradual discharge of the particles by the radiation employed. The increase in viscosity which follows is due to the aggregation of the particles, which are no longer kept apart by their mutual electrical repulsion. There is no doubt that the radiation plays some part in this aggregating process. We have found, for example, that a cerium sol which has had its viscosity reduced to the minimum value by exposure to X-rays will remain fluid for at least 24 hours if the exposure is discontinued, but will set to a firm gel if the exposure is continued for another half hour, and effects of the same kind are also shown when beta-rays are used. The curves in fig. 1 might thus be interpreted as showing that there is a numerical equivalence between the action of X-rays and that of beta-rays as far as the discharge of the colloidal particles is concerned, but that the aggregating powers of the two types of radiation are different.

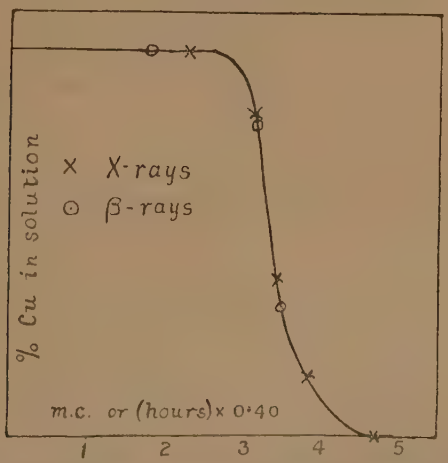
The latter conclusion is, however, hardly justifiable on the experimental evidence, for two reasons. In the first place the exposures to beta-radiation occupy a considerably longer time than the X-ray exposures, so that the process of aggregation, which proceeds at a definite rate, has a greater chance to come into play. A second disturbing factor lies in the difference in absorbability of the two kinds of radiation. Rather less than half the X-radiation was absorbed in the thickness of sol used in the experiments, but nearly 90 per cent. of the beta-radiation was absorbed. The layers nearest the emanation bulb would thus be exposed to radiation ten times more intense than those furthest away, an effect which would be still further accentuated by the geometry of the apparatus. While diffusion and convection would no doubt do much to neutralize this inequality, it seems probable that when the discharge of the particles was approaching completion those close to the emanation tube would become completely discharged, and being in an intense stream of radiation aggregate rapidly, before those which were further away had lost all their charge. The mean viscosity of the liquid would thus be appreciably increased, and would never fall to the value indicating complete discharge. The question as to the equivalence of the coagulating effects must therefore be regarded as open. What the experiments do show clearly is that there is a constant ratio between the quantity of X-rays

and the quantity of beta-rays required to produce a given decrease in viscosity in the sol.

§ 3. *Experiments with Colloidal Copper.*

Similar experiments were carried out with a Bredig solution of copper. As this sol is very sensitive to minute traces of contaminating substances, the beta-ray exposure was made in the same way as the X-ray exposure ; that is to say, in a quartz dish hermetically sealed under a glass cover-slip. The emanation bulb was simply placed on the cover-slip. The effect of the radiation was estimated by measuring the percentage of copper remaining in solution

Fig. 2.



Percentage of copper remaining in solution after exposure to varying does of X- and β-rays.

after exposure. The two curves in this case coincide exactly, within the limits of experimental error, as shown in fig. 2, where the crosses indicate X-ray and the circle beta-ray exposures. The scale of abscissæ have, of course, been chosen to bring the two curves into coincidence at one point.

The experiments with copper are not affected by the conditions which complicated those with the cerium sol, since a copper particle, when discharged, is simply precipitated, and the time element does not come into account. These experiments bring out very clearly the equivalence between the discharging effects of the two types of radiation.

A further set of experiments was made in which cerium sol was exposed under conditions identical with those used for the copper sol, with a view to ascertaining whether either of the sols showed any selective effect towards the two kinds of radiation. It was found that with this disposition of the emanation tube an exposure of one hour to the beta-rays was equivalent to a dose of 0·39 mc. of X-rays. For the copper sol, under identical circumstances, an exposure of one hour to the beta-rays produced the same effect as a dose of 0·40 mc. of X-radiation. The ratio of the beta-ray to the X-ray effects is thus independent of the nature of the solution within the limits of experimental error.

§ 4. *The Relative Energy expended by X-rays and Beta-rays in the Sol.*

The final step in the comparison between the action of X-rays and beta-rays on the colloid is some estimation of the relative energy expended by each in the sol. Thus, assuming that with the arrangements adopted in the earlier section of the paper an exposure of one hour to the emanation is equivalent to a dose of 0·62 mc. of X-rays, how do the energies absorbed in the sol during these equivalent exposures compare?

It is possible to make this comparison if we assume that the energy spent in producing a pair of ions in air is the same for both types of radiation, an assumption for which there is some experimental evidence. Our experiments showed that at the standard time the beta-rays from the emanation allowed the passage through the ionization chamber of 0·091 microcoulomb of charge. The distance of the emanation tube from the window of the chamber was, however, only 8·3 cm. as compared with 10·75 cm. for the source of the X-radiation. If the emanation tube had been placed in the same position as the focus of the X-ray tube, the charge passing through the chamber in one hour would have been $0{\cdot}091 \times \left(\frac{8{\cdot}3}{10{\cdot}75}\right)^2$, or 0·054 mc. Allowing for the absorption of the beta-rays in the air between the emanation tube and the chamber, which amounted to 6 per cent., we arrive finally at the value of 0·058 mc. per hour.

For beams of different absorbability the relative ionization currents do not give an immediate comparison of the energies of the beams. It is necessary to take into account also the relative absorptions. The ionization method of comparing

the energies of heterogeneous beams of radiation has been discussed in detail in a recent paper by Dr. Bond and myself [6], and it is unnecessary to recapitulate the argument. It can be shown that the only reliable comparison is provided by the total ionization produced by the complete absorption of the beam. The total ionzation is given by the expression $\frac{I_0}{\Delta_m} . \alpha$, where I_0 is the measured ionization in a volume of gas of which Δ_m is the mass per unit area, and α is the area of the absorption curve for the radiation in air, or some equivalent substance. If the energy spent per ion in air is constant, this expression is a measure of the energy of the beam.

Assuming a uniform distribution of radiation round the source, the energy passing into the sol is proportional to the solid angle Ω subtended by it at the radiator. Of this only a fraction f is absorbed, the remainder being transmitted. The energy absorbed in the sol is thus given by

$$k \frac{I_0 \alpha}{\Delta_m} . f . \Omega,$$

where I_0 is the charge collected by the ionization chamber during the exposure, and k is a constant.

To evaluate this expression it is necessary to obtain absorption curves for the radiation in air, and in the sol. The measurement of the absorption curves for air for the X-ray beam was described in an earlier paper [6]. For the beta-radiation the absorption curve was measured with water as the absorbing substance, as the direct measurement of the absorption curve for air presented great experimental difficulties. This substitution appears to be justifiable in the case of beta-radiation, since its mass absorption coefficient differs very little for elements of low atomic number. Absorption curves were also determined for the sols employed, from which the values of f could be determined.

Turning now to the experiments on the ceric hydroxide sol of § 2, the solid angle subtended at the focus of the X-ray tube with the dish at a distance of 3·2 cm. was 0·205. The corresponding angle in the case of the beta-ray exposure was taken as 2π. This seems to be justifiable from the symmetry of the arrangements. Experimentally an exposure to X-radiation which liberates 0·62 mc. in the ionization chamber is equivalent in its effects on the solution to one hour exposure to beta-radiation, which in turn would have produced a charge of 0·058 mc. in the chamber. The mass of air in the chamber is the same for both. So also is the

constant k, if we assume that the energy required to produce a pair of ions in air is the same for X-rays and beta-rays, an assumption which seems probable and for which there is some experimental evidence [6].

The necessary data are collected in Table III. The last column of the table contains the relative energies of the two kinds of radiation required to produce the same decrease in viscosity of the cerium sol. It will be seen that they agree to an accuracy of about 6 per cent. This is certainly within the limits of our possible experimental error. Thus, to this degree of accuracy, we conclude that the energy which must be absorbed in a given volume of sol to bring about a given loss of charge by the colloidal particles within it is independent of the nature of the ionizing radiation. The results described in § 3 clearly enable us to extend this conclusion to the copper sol.

The effect of the gamma-radiation has not been taken into account in the calculations. It must, however, be quite

Table III.

	I_0.	a.	f.	Ω.	Relative energy.
X-rays	·62	·89	·45	·205	0·050
β-rays	·058	·148	·87	6·28	0·047

small. The energy of the gamma-radiation is known, from the thermal measurements, to be about twice that of the beta-radiation. Its coefficient of absorption in water is, however, so small that the energy absorbed from it in the sol would not amount, at most, to more than one per cent. of its total energy, and its effect must therefore be very small. Its effect, if any, would be to increase the energy expended in the sol during the beta-ray exposures, and thus to bring the two results into closer agreement. To insert a correction of this order of magnitude, however, would give the experiments an air of accuracy to which they can lay no claim.

In concluding this part of the paper, I should like to take the opportunity of thanking Professor S. Russ for supplies of radon, and Mr. J. A. V. Fairbrother for assistance in the experimental part of the work.

§ 5. *Discussion of Results.*

The result arrived at in the last section, that the loss of charge by the colloidal particles is proportional to the energy

absorbed in the solution, while not in itself affording us a basis for a theory of the action of ionizing radiations on colloidal solutions, at least enables us to rule out certain possibilities. The absorptions measured in the experiments were absorptions in the sol as a whole, that is mainly in the solvent, since the amount of colloidally-dispersed substance in the sol is too small to affect the absorption much. Now, this will be very different from the absorption of the radiation of the colloid particles. The mass coefficients of X-ray absorption for copper and cerium are about forty times that of water. For beta-radiation, however, the ratio is of the order of two to one. It is clear, then, that for equal absorptions by the sol as a whole the absorption of X-rays by the colloid will be far greater than that of beta-rays, in the ratio, in fact, of nearly twenty to one. The effect on the colloid is, however, practically the same in both cases. Hence the change in the colloid particles must be due to the action of the rays on the solvent, and not a direct action on the colloid particle itself.

Again, the primary effect on the absorption of X-rays is the production of photo-electrons. For an equal absorption of energy the number of these photo-electrons generated will be far greater than the number of beta-particles passing through the solution. We cannot therefore associate the action on the colloid particle with the starting or stopping of a high-speed electron. These considerations seem to show that the "hot spot" theory, which Dessauer has put forward to account for the action of the rays on biological material, are not applicable to colloidal solutions, as a "hot spot" formed in the mass of solvent would hardly retain its high temperature long enough to act on the comparatively large mass of a colloid particle. We are, I think, compelled to look for the cause of the coagulation of the colloids in the one effect which the two types of radiation have in common—the production of ions in the solvent. We have already put forward this suggestion in previous communications. The experiments we have just described provide additional confirmation of our suggestions.

6. *The Action of Ionizing Radiations on Colloidal Solutions.*

There still remains the problem as to whether the discharge of the sol is an immediate effect of the ionization, or whether the ionization brings about some chemical or other change in the medium, which in turn brings about the precipitation of the colloid from solution. Fernau and

Pauli [4] have suggested that the primary effect of the radiation is the production of hydrogen peroxide in the solution, which then coagulates the colloid in the usual way. It is, perhaps, somewhat difficult to disprove this hypothesis, but the following results seem strongly against it :—

(*a*) As has already been reported, exposure of pure water to varying doses of X-radiation does not produce an amount of hydrogen peroxide which is detectable even by the most delicate tests.

(*b*) Experiments recently made in the laboratory show that hydrogen peroxide in dilute aqueous solution is readily decomposed by exposure to X-rays. This result is confirmed by recent experiments of Glocker and Risse [7], who have studied the action quantitatively.

It might, however, be possible to hold that, under the action of the radiation, there is an equilibrium at some very minute percentage, between the water and the hydrogen peroxide, which is maintained by the radiation as the minute traces of hydrogen peroxide present are absorbed by the colloid. To test this somewhat elaborate hypothesis, Bredig solutions of copper were made by sparking between copper rods under ethyl alcohol, and under amyl alcohol. The colloidal copper was precipitated from both these organosols by exposure to X-rays. They were, in fact, decidedly more sensitive to the radiation than the corresponding water sol. It is true that both alcohols would probably contain traces of water, but one would have expected that, with the very small amount of water present, the exposure necessary to produce the amount of hydrogen peroxide required for coagulation would at least have been very much prolonged. Colloidal solutions of silver resinate in oil of lavender and in benzene were also affected by X-rays. Here the amount of water present, if any, must have been very small. On the evidence, then, it seems much more probable that the effect is a direct one, and that the colloidal particles have their charges neutralized by the ions formed in the double layer round them.

There remains the fact, for it seems to be a fact, that only sols in which the particles are positively charged are coagulated either by X- or beta-radiation. Hardy [4], for example, found that positively-charged globulin was coagulated by beta-radiation, but negatively-charged solutions of the same substance were unaffected. Wels and Thiele [8] report the same result, using X-radiation. In the course of the last two years we have examined a large number of

sols, with the result that in no case have we been able to coagulate a negatively-charged colloid, and in no case have we failed to produce coagulation where the particles of the sol were positively charged. With sols, such as silver iodide, which can be prepared with the particles either positively or negatively charged, the former are coagulated, the latter are apparently unaffected by the radiation.

It seems to me that the one-sidedness of the effect may be connected with the different nature of the initial positive and negative ions. The positive ion is never smaller than an atom. The negative ion begins as a free electron, and in a gas persists in this state for an appreciable fraction of its existence. Our knowledge of the behaviour of ions and electrons in a liquid medium is very scanty, but it is not improbable that a similar state of affairs exists there also.

We now suppose that the colloid particles are surrounded by a closely adherent film of molecules of the solvent. There is considerable evidence in favour of the view that the surface along which slip takes place when the particle moves under a field is entirely within the solvent and not between the solvent and the particle, and Fairbrother's observation that the size of the colloidal particles decreases as they lose their charge is additional evidence in favour of the supposition. If the colloid is electro-negative it attracts the positive ions formed by the radiation in the double layer surrounding it. The positive ion, however, being molecular, will be unable to penetrate the protecting skin of solvent molecules which surrounds the colloid particle, and remains outside, where it is either neutralized or takes the place of one of the electrolytic ions which form the outer shell of the double layer.

If, however, the particle is electro-positive, so that it attracts the negative ion, the latter, being in an electronic state, and being in an electric field of the order of 10^5 volts per cm., will be able to penetrate the protective skin of solvent molecules and so to neutralize the charge on the particle itself. An alternative suggestion, which experimentally is probably indistinguishable from the first, is that the electron by entering an atom on the outer face of the skin causes the liberation of an electron from an atom on the inner surface in contact with the particle. We have not at present sufficient knowledge to enable us to apply numerical tests to this hypothesis. It seems, however, to be the one which most adequately explains our experimental results on the action of ionizing radiations on colloidal solutions.

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Department of Physics,
University of Reading,
Oct. 27, 1928.

IX. *On the Intensities of some Fe^+ Multiplets in the Arc and Chromosphere Spectra.* *By* William Clarkson, *Ph.D., M.Sc., International Education Board Fellow, Physical Institute of the University of Utrecht* *.

Introduction.

RECENT work of Professor Ornstein and T. Bouma [1] on the intensity relations in the multiplet spectra of nickel and cobalt having led to interesting extensions of the multiplet summation rules, the writer undertook, at the suggestion of Professor Ornstein, some intensity measurements on the multiplet spectra of ionized iron. On determining the intensities for the two multiplets selected, $2^4F-2^4F'$ and 2^4F-2^4D respectively, it was not only possible to compare their variations with the ones predicted by theory, but also to compare them with the ones for the solar emission ("Flash") spectrum, these having been determined during the recent Dutch Eclipse Expedition to Lapland in 1927 [2].

Measurements.

The initial source of spectrum was the middle-fifth of an arc between rods of ordinary iron. The grating used being stigmatic, the convenient step-weakener method of intensity measurements was employed.

To keep ionic concentration, and thus self-reversal, as small as possible it was desirable to use the smallest current practicable. It was found that a current of two

* Communicated by Professor Ornstein.

amperes could be used, as it gave just the same results as the less convenient minimum of about one-half ampere. That the self-absorption would be expected to be small in both cases was suggested by the very low intensities of the lines.

Owing to "blending" with nickel and cobalt lines probably having an influence in two critical cases, those of lines 4520 and 4549, the measurements were repeated using poles of electrolytic iron; in this case cobalt was absent and nickel, if indeed present, a mere trace. It was found that, allowance being made for the small effect of these two blends, the results for the two plates were the same.

Results.

The two plates, for ordinary and for electrolytic iron, were photometered several times and the intensities of the lines and of the background were determined. Although analysis of the photograms was necessary in the case of several lines, the results were quite definite.

The background was found to present the one likely source of error. The apparent background, at least, was neither constant, nor did it vary regularly with wave-length. At intervals throughout the plate, however, the background appeared quite line-free and homogeneous, and it was found that for these points the photograms recorded a constant and minimum intensity. Since we cannot allow for the unknown bands or lines which presumably might have introduced blending, and the apparent background had dubious significance, and since in any case local homogeneity would have had to be assumed, the line intensities have been derived, assuming the minimum background to apply throughout the plate. That even in the doubtful cases the error would appear to be negligible is shown by the consistency of the results in comparison with those for the chromosphere.

Table I. tabulates the theoretical intensities with those for the arc and the flash spectra, and with the visual estimations quoted by Russell [3] (for laboratory conditions, but source not given).

Fig. 1 expresses the relation between the theoretical intensities and those for the arc and flash respectively in a graphical form. The log scale is used so that slopes may more readily be compared. The lines joining the points are generally without significance, and are given to stress their general relation and heir erraticity.

Some remarks on the flash results are necessary. In these, two determinations of the intensities, *a* and *b* respectively, using different methods were made. It was found that the application of a conversion factor served to convert *b* into *a* values, and that then the values generally coincided. Some differences, however, were encountered ; in these cases both values are given. The mean has not been given, as the

TABLE I.

	λ.	Inner Quant. No.	Intensities (units arbit.).			
			Theo.	Flash, *a* & *b*.	Arc.	Russell.
$^4F-^4F'$.	4472	3—2	168	28, 20	6	—
	4489	4—3	225	32	10	4
	4491	2—2	472	41, 27	12	4
	4515	3—3	867	46, 51	20	6
	4520	5—4	175	49	66	6
	4534	2—3	168	25 (prob.).	7	—
	4555	4—4	1280	59	24	6
	4582	3—4	225	21	6	—
	4629	5—5	1925	76, 60	25	4
$^4F-^4D$.	4508	2—1	245	42	14	8
	4522	3—2	392	64	25	6
	4541	2—2	98	27, 24	7	—
	4549	4—3	600	? 50 ?	60	4
	4576	3—3	128	25, 22	8	4
	4583	5—4	875	80, 102	28	8
	4620	4—4	100	19	5	—

probability is that one of the results is the true one, the other being erroneous. Fig. 3 supports this conclusion and provides the weighted values employed in fig. 1.

The flash intensity of the line 4549 remains doubtful, as its intensity cannot be freed from the effects of blending with the much more intense Ti^+ line. It can be awarded a minimum intensity of about 40, and since the peaks of the lines do not coincide, probably of about 50 (the value used.

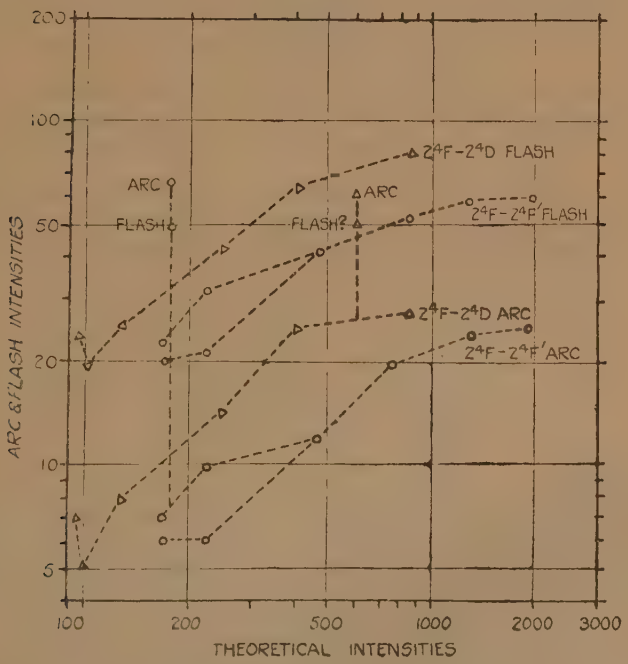
here); but the purely speculative nature of these, and the fact that there must be abnormal self-reversal due to the influence of the titanium, prevents quantitative comparisons with the corresponding arc line being possible.

Discussion.

1. *Comparison with Theoretical Multiplet Rules.*

It will be seen (fig. 1) that there is a close general resemblance between the curves for the same multiplet, but that

Fig. 1.



however these measured values for the arc and flash agree among themselves, they show little correlation with the theoretical intensities. This disparity is exhibited most markedly in the case of one line in each multiplet. The first line, 4520, is also highly abnormal in the flash spectrum, though not to such a great extent as in the arc; unfortunately the second, 4549, is the line of doubtful intensity. It is interesting that the value allotted it makes it abnormal in

the flash in a reverse direction; but one cannot build on this, as it might easily be the result of the abnormal self-reversal previously mentioned.

That there are well-established, if at present little understood, causes of deviation inherently present in complex electronic systems immediately suggests the explanation of those found here, should it be found that they are not due to such a factor as self-reversal.

For this we may compare the results in two ways :—(*a*) The arc and flash results with the multiplet summation rules, particularly those recently established for the equally complex cases of nickel and cobalt (this will check the results from a theoretical standpoint [1]); and (*b*) the arc results with the

TABLE II.

		$2^4F'$.				2^4D.				Summations.		
		2	3	4	5	1	2	3	4	Theo.	Arc.	Flash.
2^4F.	2	12	7			14	9	×	·	990	$^{19}40^{21}$	132
	3	6	20	6			25	8	×	1785	$^{32}65^{33}$	181
	4		10	24	?6			60	5	2380	$^{40}105^{05}$	183
	5			66	25				28	2975	$^{91}119^{28}$	189

emission ("flash") spectrum of the chromosphere (here there should be no effect due to abnormal conditions of excitation, and certainly an effect due to self-absorption [2]).

2. *Comparison with Theoretical Summation Rules.*

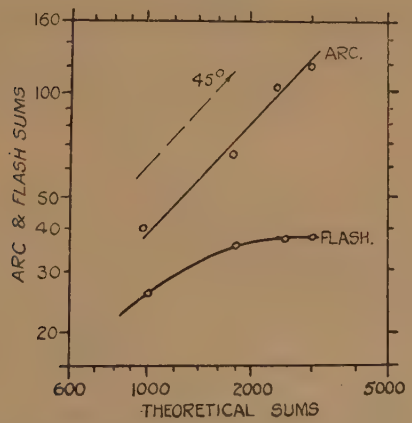
Table II. presents the intensity scheme for the arc, with total summations for the theoretical intensities and for the arc and flash. On the one hand the sums of the individual multiplets are found to exhibit no correlation with those predicted, on the other the total sums will be seen to be in excellent accord.

Intensity measurements have previously revealed that in several cases, though the theory did not meet the case of the individual lines, it agreed with the sums quite well. More

recently [1] it has been shown, from the cases of nickel and cobalt, that even this might not apply, but that again an extension of the rules, this time to the total sums of each system of two or four multiplets, brought about correspondence. Table II. shows that the multiplet spectrum of ionized iron must be included under this category.

How close this linear relation is, the lines of "abnormal" intensity notwithstanding, is well shown in fig. 2. Indeed, with respect to the two normal lines, we see that it is only their great virtual irregularity which caused the close correspondence between the total sums to be preserved.

Fig. 2.



The results for the flash, which show corresponding individual variations to those for the arc, are equally illuminating, for even though here the total sums do not correspond to the theoretical ones at all, yet their curve also is continuous, thus showing that a close correlation exists. Indeed, we should expect a curve of this form to show the expected self-reversal of the solar spectrum, whilst the 45° slope of the arc curve justifies our opinion that self-absorption is inappreciable in its case. The total sums thus give the insight into the true phenomena apparently denied by the individual results.

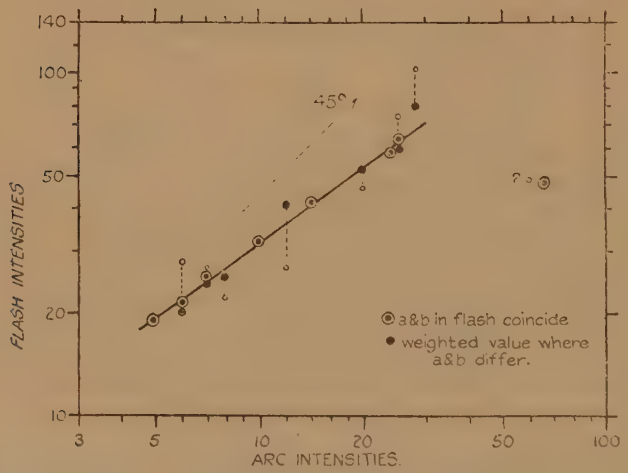
3. *Arc-Flash Comparison.*

Should the deviation of measures from theoretical values in the case of the intensities of individual lines be due, as

suggested, to the inadequacy of the theory, and should the arc be free from self-absorption, we may accept the intensity values for the latter as the legitimate supplanters of the theoretical ones. In this case, since self-reversal would appear to be the only additional factor operating to modify the chromospheric intensities, the arc and flash spectra should show a correlation extending to the individual lines.

Fig. 3 shows the relations between arc and flash values. The incontrovertible points lie on a straight line, with slope less than 45°, and of the doubtful points the suggestion that one of each pair would probably be valid appears to have

Fig. 3.



been warranted. This result is most satisfactory. In connexion with the form of the graph, it is instructive to note that when all the points for the series of ionized iron multiplets are plotted against the theoretical values a similar straight line (though of somewhat different slope) is found to apply.

There is, however, one serious divergence from this relation, and this is of a disturbing nature ; the two lines of particularly abnormal intensity, 4520 and 4549, give points lying a long way off the curve. In attempting an explanation, all we can scrutinize is the validity and significance of the flash intensities, for in view of the evidence we must assume that the lines actually do belong to the multiplets, and the arc values may be taken as basis.

There can hardly be errors of an observational nature, and blending would serve but to exaggerate the divergence; yet to fit the points to a linear relation would demand the increasing of the observed intensities of 50–60 to about 120–30; fitting them to the maximum curve possible would only reduce this to 90 or so. It is not impossible that these lines, having abnormal intensity, may also be subject to abnormal self-reversal; but though this is a quite plausible assumption, the data available do not permit us to proceed so far with correction. In the circumstances the problem of these lines must be left as presented, as an experimental fact.

The writer is greatly indebted to Professor Ornstein, at whose instigation this problem was taken up, and to Dr. Minnaert, of the Heliophysical Department, for the furtherance of this research, and to the International Education Board for the Fellowship, during the tenure of which this work was carried out.

Summary.

Results of intensity measurements of the multiplets $2^4F - 2F'$ and $2^4F - 2^4D$ for ionized iron, for an iron arc, and for the chromosphere ("flash" spectrum) are treated. Both show similar wide divergencies from theoretical intensities of individual liues; one line in each multiplet is particularly "abnormal."

Comparisons of multiplet summations show :—

(*a*) In ionized iron, as in nickel and cobalt, the multiplet summation rules only apply when extended to the total sums of the two multiplets (Ornstein and Bouma).

(*b*) The arc is free from self-absorption, and thus gives the fundamental line intensities. The flash sums demonstrate self-absorption.

The flash-arc relation is linear, but the two very abnormal lines lie off this curve. This is briefly discussed.

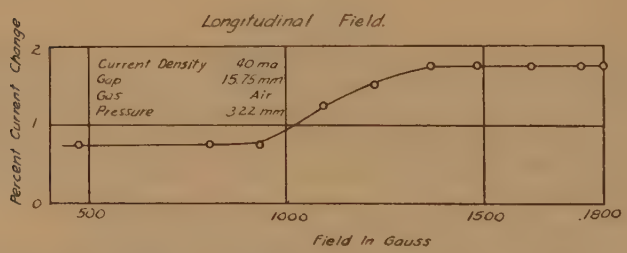
References.

(1) Ornstein & Bouma (pending).
(2) Pannekoek & Minnaert, *Kon. Akad., Amsterdam,* part 13, no. 5 (1928).
(3) Russell, Ap. J. lxi. p. 223 (1925).

X. *Control of Current in a Discharge-Tube by Means of a Magnetic Field.*—*By* Robert F. Earhart *and* Charles B. Green *.

In certain experiments involving the discharge of electricity through gases, moderately high potentials are required to produce and maintain a discharge. Control of current through the circuit is usually effected by variable resistances in the circuit. On page 481 of 'Conduction of Electricity through Gases,' Sir J. J. Thomson describes an experiment in which it was desired to alter the current in the circuit without varying the impressed e.m.f. or disturbing the ordinary constants of the circuit. For this purpose a Wehnelt cathode was used in a spark gap and this was placed in a longitudinal magnetic field. Variation in the current passing through the circuit was produced by

Fig. 1.



altering the field. This has the effect of introducing a "valve" into the circuit, one which may be regulated by a control outside of the circuit proper.

One of us † had previously made some experiments on the effect of applying a magnetic field across a discharge gap under a limited range of conditions. In connexion with some extensions of the experiments, we have been led to study the extent of such valve control and the optimum conditions for applying it. Instead of using a Wehnelt cathode, a discharge was produced between plane, parallel, brass plates at ordinary temperatures. It was found that, if the distance between such electrodes was several cms., an increase in the current was produced upon applying a longitudinal field, but that this effect was small, especially for a current of several milliamperes. It was found further that if the

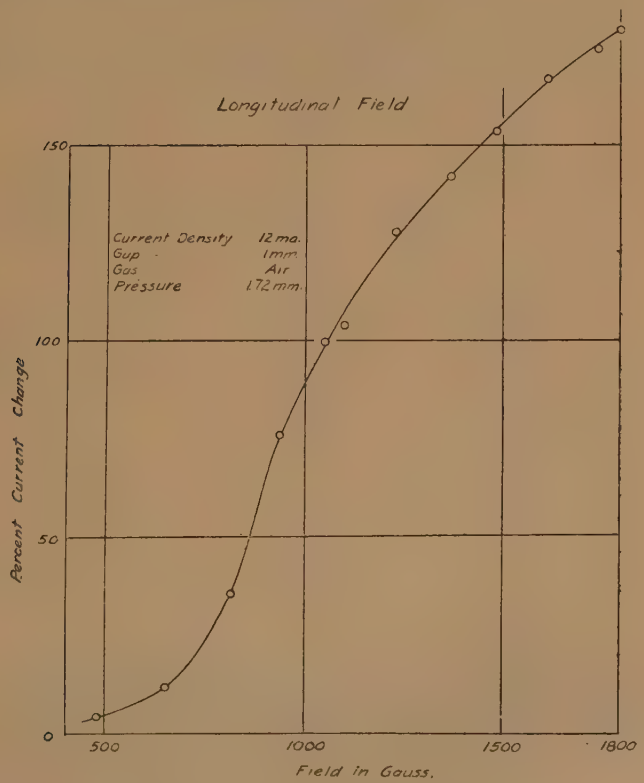
* Communicated by the Authors.

† Robt. F. Earhart, 'Physical Review,' Aug. 1914.

distance between the plates was reduced to the order of 1 mm. and the pressure properly adjusted, variations in current produced by varying the field might be as much as several hundred per cent. Figs. 1 and 2 indicate the extent of such a change.

Attention is called to the difference in scale used to show the percentage change.

Fig. 2.

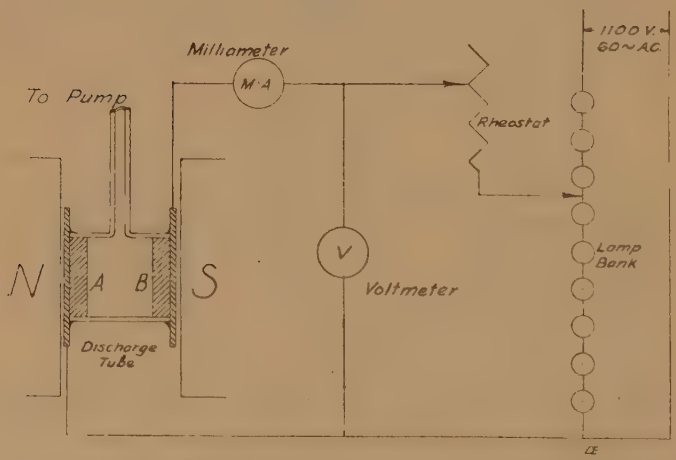


The accepted explanation for the increase in current under the influence of such a field, is that increase in ionization by collision occurs due to the helical motion of such ions as initially have a velocity component perpendicular to the electric force. Possibly this might give rise to another effect which would limit or even cause a decrease in the current, viz., that the ions which execute such motion might spiral out of the path between the electrodes and be dispersed

to the sides of the supporting tube. Our experiments can be interpreted if both effects exist.

A. W. Hull* published a paper in which a study was made of similar effects. A part of his paper dealt with a radial discharge of electrons produced from an incandescent wire to an outer co-axial cylindrical electrode and with a magnetic field applied parallel to the axis of the tube, thus giving a transverse field. The experiment was made in high vacuo so that it could be assumed that the mean free path of the electron was greater than the distance between the electrodes. This type of problem is amenable to calculation, and he found good agreement between the computed distribution

Fig. 3.



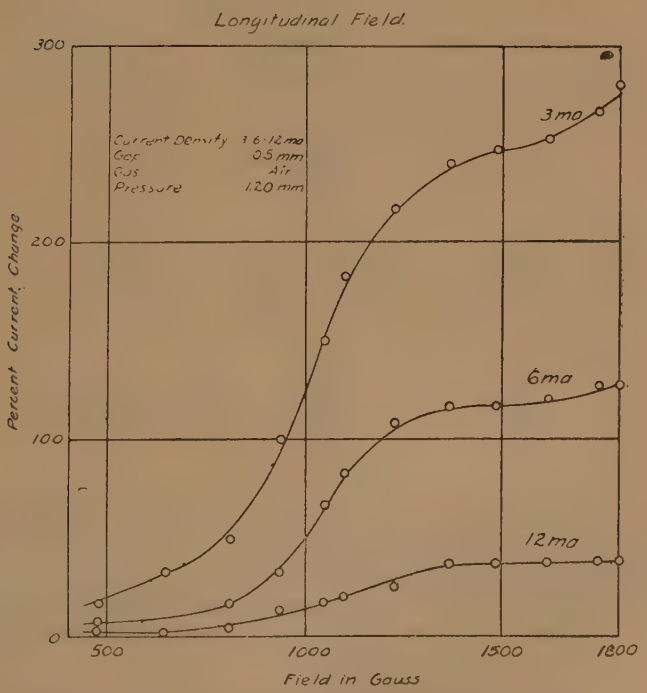
of electron current and the measured values. The experimental conditions of our experiment preclude simplifying assumptions either as to mean free path or for unsaturated currents. Ions formed in air are complex in character, and in no case was the mean free path small compared with distance between electrodes; moreover, if increase in ionization is caused by increase in path due to the helical motion of an ion, then, when a collision occurs, the new ions thus formed would tend to execute a spiral motion starting from the point at which they originate.

The possible results are not amenable to calculation by any methods with which the authors are familiar.

A. W. Hull, 'Physical Review,' July 1921.

Fig. 3 indicates the arrangement of the apparatus used. A transformer stepped up 60-cycle A.C. current to 1100 volts which was sent through 12 lamp filaments in series. By tapping off from these and introducing a liquid rheostat, suitable e.m.f.'s could be applied to the electrodes A and B placed in a discharge chamber and the initial currents regulated. The electrodes were cut from a brass rod 1·8 cm. in diameter and fitted closely in a glass tube. The discharge

Fig. 4.



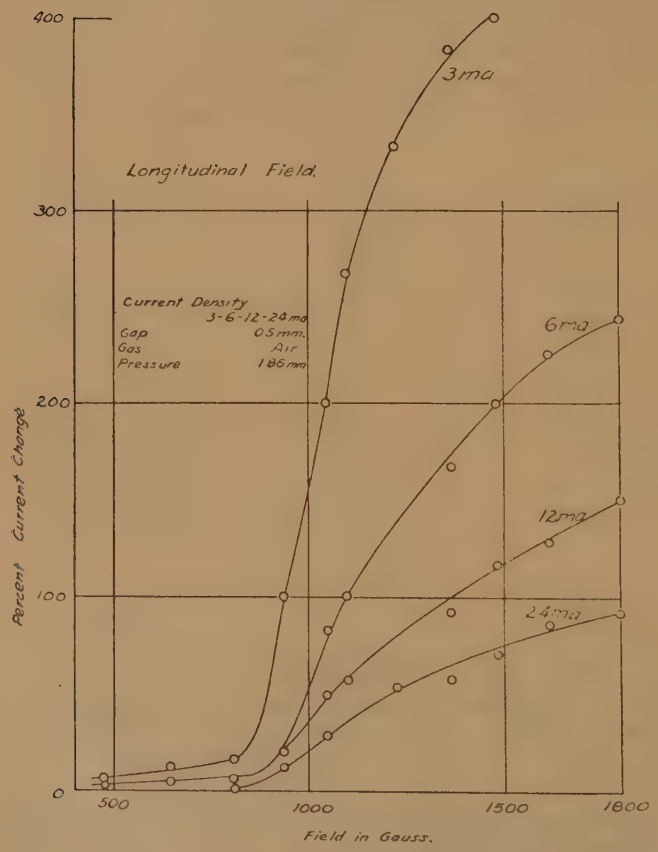
chamber was placed between the poles of an electromagnet provided with large flat pole-pieces. The magnetic field was calibrated and explored by means of a flip coil in the usual manner.

It was soon found that variation in the current effected by altering the magnetic field depended on the magnitude of the current passing across the gap. A failure to recognize this as one of the variables is possibly responsible for lack of agreement between results reported by different observers.

There appear to be at least three variables which will modify the changes produced by application of the field :—

(1) Distance between electrodes.
(2) Pressure of gas in the chamber.
(3) Magnitude of the current under stress.

Fig. 5.



Figs. 4 to 6 inclusive show the character of changes produced when the distance between the electrodes is small.

Referring to fig. 4, it appears that the larger currents, *i. e.*, those of 6 and 12 milliamperes, are less changed by the field than the 3 milliampere current. Indeed, for larger currents rather moderate fields produce a condition such that further

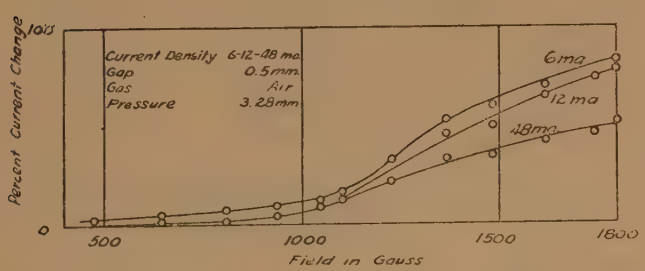
increase in field strength does not add much to the change. This relation appears in each of the families of curves in figs. 5 and 6. This "saturation effect" applies equally well to the smallest current which we have used but for higher values of the magnetic field than shown in the graphs.

Fig. 6 indicates the extent to which control is reduced with increase in pressure. The general inference is that the maximum control by the longitudinal field is obtained for small currents, through small distances, and at a pressure near the critical pressure.

Experiments with hydrogen afforded families of curves of the same type as those for air.

A series of experiments was made with one electrode a point, the other a plane. It is well-known that for pressures of the order used, ·5 mm. to 5 mm., there is a large factor of

Fig. 6.



rectification of an A.C. current. This rectified current was measured by adding a D.C. milliameter to the circuit. The unidirectional current was affected by the magnetic field in much the same way as the sinusoidal current. Graphs for this are omitted.

Experiments with Transverse Fields.

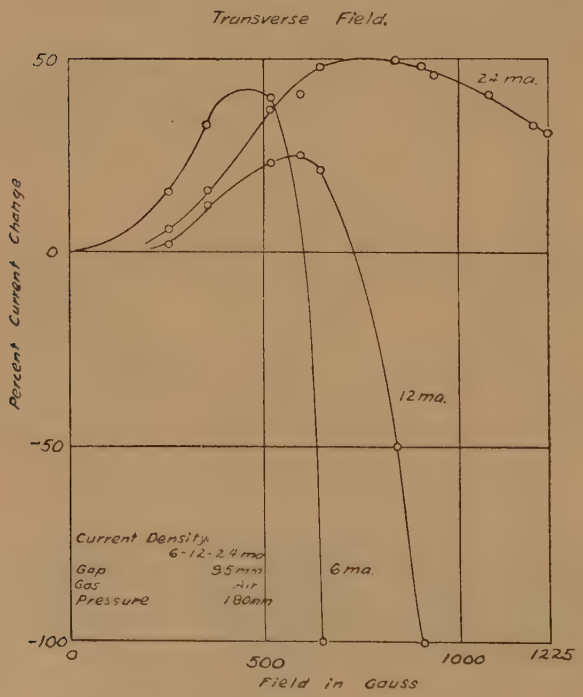
It is generally assumed that the application of a transverse magnetic field will diminish the current flow across a discharge gap and ultimately extinguish it, if the field intensity is sufficiently great. Indeed, the magnetic blow-out of an arc is a well-known application of this phenomenon.

Our experiments show this to be the case if the distance between the electrodes is large (5 cm.), or the pressure exceeds a few mm. J. E. Ives * noted an exception to this

* J. E. Ives, 'Physical Review,' Oct. 1918.

commonly observed fact. He found that a current of 1 milliampere which passed between electrodes under a pressure of ·18 mm. was increased by a transverse magnetic field. Our experiments confirm Ives' experiment. Especially is this the case when the distance between the electrodes is small. The helical motion of an ion spiraling along a line of magnetic force would increase ionization by

Fig. 7.



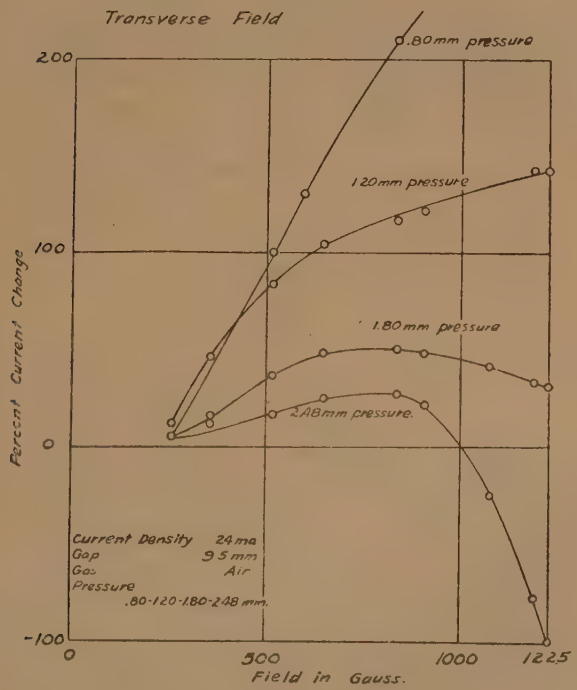
collision, and this might be quite effective in augmenting the current, especially if the area of the electrodes was large compared with the distance separating them.

We have found that, for small distances and pressure properly adjusted, fields of a few hundred gauss may considerably increase the current, while larger fields may reduce the current. Current density again appears as a variable, as was the case with longitudinal fields. This effect is represented graphically in fig. 7.

Fig. 8 indicates the part that pressure plays in these variations. The initial current, *i.e.* with zero field, was 24 m.a. in each case. This shows that the percentage change produced by field is diminished with increase in pressure. In fig. 9 the extent to which changes in length of gap affect the variation is shown.

In one of our experiments the electrodes were separated 5 cm. and a uniform glow produced in the tube with the

Fig. 8.



field off. The axis of the tube was horizontal, likewise the lines of magnetic force were horizontal and perpendicular to the electric force. Upon applying a small field, the discharge was broken up into transverse striæ which appeared at the top and bottom of the tube, while the core and sides were free from luminous striations ; this might be expected by applying the Fleming left-hand rule. As the field strength was varied, the striations could be made to

Fig. 9.

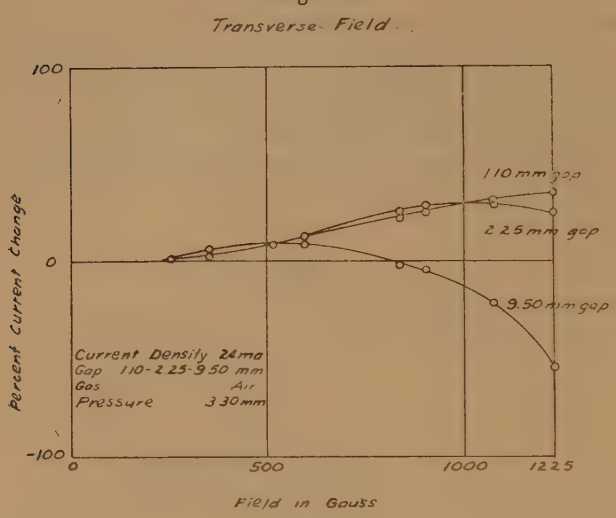
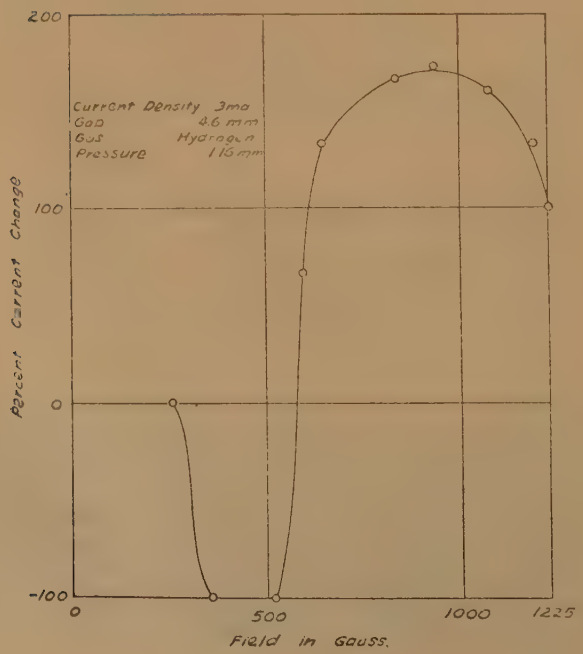

Transverse Field
100
0
-100
Percent Current Change
1.10 mm gap
2.25 mm gap
9.50 mm gap
Current Density 24 ma
Gap 1.10-2.25-9.50 mm
Gas Air
Pressure 3.30 mm
0
500
1000
1225
Field in Gauss

Fig. 10.


Transverse Field.
200
100
0
-100
Percent Current Change
Current Density 3 ma
Gap 4.6 mm
Gas Hydrogen
Pressure 1.15 mm
0
500
1000
1225
Field in Gauss.

progress back and forth, but with increase in field were crowded against the walls of the tube until extinction occurred.

There is a critical region of pressure and distance where the form of these graphs alters. In some experiments with hydrogen, it was found that a magnetic control could be effected where small fields would decrease the current quite uniformly to 50 or 60 per cent. of the original value, while larger fields restored and even increased the current by more than 100 per cent. (fig. 10) shows an extreme case where the application of a transverse field of from 300 to 500 gauss extinguished the discharge, while slightly higher fields restored it, and an application of 1000 gauss more than doubled the current. The application of still higher fields reduced the current finally to the point of extinction and here the extinction was final.

Mendenhall Physical Laboratory,
Ohio State University, U.S.A.,
June 1928.

XI. *On the Condenser-Telephone.* *By* G. Green, *D.Sc.*, *Lecturer in Physics in the Applied Physics Department of the University of Glasgow* *.

IN a former paper under the above title which appeared in the Phil. Mag., Sept. 1926, pp. 497–508, a preliminary discussion is given of the mathematical theory of the condenser-telephone. The discussion there given is, however, limited to a special case, namely, that of a condenser consisting of two plates only separated by a dielectric sheet of elastic material, one of the plates being regarded as fixed and the other as free to move in response to electrical vibrations transmitted to the condenser circuit. The condenser circuit is understood to consist of a transformer secondary coil of inductance L and a battery of e.m.f. E in series with the condenser, the total resistance of the circuit being R ; and the problem considered in the earlier paper is to determine the motion of the free plate of the condenser when a small periodic e.m.f., $e \sin \omega t$, is applied to the circuit by means of the transformer. For certain purposes the two-plate condenser-telephone is worthy of study, but the case of a condenser consisting of a pile of plates of which one only,

* Communicated by the Author.

the undermost plate, is regarded as fixed, while all the others are free to move in response to electrical vibrations, is more important, as condensers of this type are likely to find more general application. The investigation of the more general case is interesting in itself, and is desirable for the satisfactory understanding of the dynamical theory of the condenser-telephone.

Consider a condenser consisting of parallel plates numbered 0, 1, 2, 3, ..., n respectively. Take plate number 0 as fixed in position in a vertical plane, while the other plates are at successive distances d, $2d$, $3d$, etc., from it, each plate being just in contact with the dielectric material which separates the plates, but not exerting any more force upon it, when the condenser is uncharged. For our purpose it is convenient to regard this whole condenser as made up of n separate condensers arranged in parallel, plates 0 and 1 forming condenser No. 1, plates 1 and 2 forming condenser No. 2, and so on up to No. n. When the separate condensers are charged each with charge Q_0 electromagnetic units, the plates are alternately positive and negative, and the uniform distance between each pair of consecutive plates is altered from d to $(d-a)$, where a is given by the equation

$$\mathrm{YA}\frac{a}{d}=\frac{2\pi Q_0{}^2v^2}{\mathrm{A}k}, \quad . \quad . \quad . \quad . \quad . \quad (1)$$

the notation employed being the same as that of the earlier paper, with Y as the Young's Modulus of the dielectric material. This equation defines the equilibrium position of the plates when each constituent condenser has the charge Q_0. The uniform charge Q_0 on each side of each plate may also be looked upon as due to the constant e.m.f. E acting between the plates. When a variable e.m.f., $e\sin\omega t$, is superposed upon the steady e.m.f. E acting in the circuit, the coordinates defining the positions and charges on the plates at any instant t can be chosen with reference to the equilibrium condition of the system. Thus we may take $x_1, x_2, x_3, \ldots, x_n$ to denote the displacements of the plates from their equilibrium positions towards the fixed plate at instant t, and Q_0+q_1, Q_0+q_2, Q_0+q_3, ..., Q_0+q_n, to denote the charges on each of the successive condensers. The sum of all the charges on all the positive plates, or on all the negative plates, is thus $nQ_0+\Sigma q$ at instant t.

We can now write down the equations of motion of the plates. The forces acting on each plate of the condenser consist of the mutual electrostatic attractions between the plate and the two plates immediately in its front and rear

respectively, together with the pressure forces applied to it by the dielectric material in contact with it on either side. Thus the equation of motion of any one of the plates, with the exception of the outermost plate, which communicates its motion to the air on its open side, is indicated completely by an equation of the type shown for plate r below :—

$$m\ddot{x}_r = \frac{2\pi v^2}{Ak}\{(Q_0+q_r)^2-(Q_0+q_{r+1})^2\}$$
$$-YA\frac{a+x_r-x_{r-1}}{d}+YA\frac{a+x_{r+1}-x_r}{d}. \quad . \quad (2)$$

Here the mass m must be taken to represent the sum of the masses of the metallic plate and of the sheet of dielectric material in contact with it on one side. In the case of the outermost plate, the reaction of the air on the open side can be represented by a resistance term proportional to the velocity $\kappa\dot{x}_n$, as we have found in the earlier investigation. Hence the equation of motion of the outermost plate becomes

$$m\ddot{x}_n = \frac{2\pi v^2}{Ak}(Q_0+q_n)^2-\kappa\dot{x}_n-YA\frac{a+x_n-x_{n-1}}{d}. \quad . \quad (3)$$

Before we can obtain the solution of these equations, the quantities $q_1, q_2, q_3, \ldots, q_n$ must first be expressed in terms of $x_1, x_2, x_3, \ldots, x_n$, the displacements of the plates. This can be done by making use of the equation to the condenser circuit itself and of certain relations which hold between the separate parallel condensers composing the complete condenser at any instant.

According to the notation employed in the former paper, if we denote by C_0 the capacity of any one of the condensers in parallel when all the plates occupy their equilibrium positions, and by C_r, the capacity of condenser r at instant t, we find that

$$C_r = C_0\left[1+\frac{x_r-x_{r-1}}{d-a}\right], \quad . \quad . \quad . \quad . \quad (4)$$

first-order terms only being retained; and also that the capacity of the complete condenser is represented by

$$\Sigma C = nC_0\left[1+\frac{x_n}{n(d-a)}\right]. \quad . \quad . \quad . \quad . \quad (5)$$

If we let $Q = nQ_0+\Sigma q$ represent the total charge upon the condenser at any instant, the equation to the condenser circuit may be written in the form

$$L\frac{d^2Q}{dt^2}+R\frac{dQ}{dt}+\frac{Q}{\Sigma C}=E+e\sin\omega t; \quad . \quad . \quad (6)$$

and in view of the relation $nQ = E\Sigma C$ and of (5) above, the equation to the circuit becomes, finally,

$$L\frac{d^2\Sigma q}{dt^2} + R\frac{d\Sigma q}{dt} + \frac{\Sigma q}{nC_0} = e\sin\omega t + E\frac{x_n}{n(d-a)}. \quad . \quad (7)$$

In this case we may assume that x_n can be represented by $X\sin(\omega t+\epsilon)$, and the solution can immediately be written down as in equations (6), (7), and (8) of the previous paper, referred to above. We have, accordingly,

$$\Sigma q = \alpha\left\{ e\sin\omega t + E\frac{x_n}{n(d-a)}\right\} - \beta\left\{ e\cos\omega t + E\frac{x^n}{\omega n(d-a)}\right\},$$

where

$$\alpha = \frac{nC_0(1-nC_0L\omega^2)}{D^2} = \frac{nC_0\cos\theta}{D},$$

$$\beta = \frac{Rn^2C_0^2\omega}{D^2} = \frac{nC_0\sin\theta}{D},$$

and

$$\tan\theta = \frac{RnC_0\omega}{(1-nC_0L\omega^2)}, \text{ and } D^2 = \{(1-nC_0L\omega^2)^2 + R^2n^2C_0^2\omega^2\}. \quad . \quad . \quad . \quad (8)$$

The additional relations which we require in order to eliminate the oscillatory charges q_1, q_2, q_3, ..., q_n, from equations (2) and (3), above are obtained from the condition that at any instant each of the separate condensers in parallel of which the complete condenser is composed, has the same potential difference $E + e\sin\omega t$ between its plates. We thus obtain the equations

$$\frac{Q_0+q_1}{C_1} = \frac{Q_0+q_2}{C_2} = \ldots = \frac{Q_0+q_r}{C_r} = \ldots \frac{nQ_0+\Sigma q}{\Sigma C}, \quad (9)$$

and as each of the terms appearing in this can be expanded as follows:

$$\frac{Q_0+q_r}{C_r} = \frac{Q_0}{C_0}\left[1-\frac{x_r-x_{r-1}}{d-a}\right] + \frac{q_r}{C_0}, \quad . \quad . \quad (10)$$

we find, finally, that

$$q_r - q_{r-1} = \frac{EC_0}{d-a}(2x_r - x_{r-1} - x_{r+1}). \quad . \quad . \quad (11)$$

For the present, in order to take the simplest case for mathematical analysis, we are assuming that all the quantities q_1, q_2, q_3, ... q_n are small compared with Q_0, and that their squares are negligible in equations (2) and (3). These

equations, by means of the results contained in (8) and (11) above, we can now write in terms of $x_1, x_2, x_3, \ldots, x_n$, and their derivatives. Instead of (2) we now have

$$\left.\begin{aligned} \ddot{x}_1 &= -c^2(2x_1 - x_0 - x_2) \;:\quad \text{with } x_0 = 0 \\ \ddot{x}_r &= -c^2(2x_r - x_{r-1} - x_{r+1}) \end{aligned}\right\} \quad . \quad . \quad (12)$$

for all values of r up to $n-1$, and

$$c^2 = \frac{\mathrm{YA}}{md} - \frac{\mathrm{E}^2\mathrm{C}_0}{m(d-a)^2}.$$

Instead of (3) the equation to the outermost plate may now be written in the simpler form :

$$\ddot{x}_n = -2\mathrm{K}\dot{x}_n - c^2(x_n - x_{n-1}) - \mathrm{A}'x_n + \mathrm{B}\sin(\omega t - \theta); \quad (13)$$

where

$$2\mathrm{K} = \left[\frac{\kappa}{m} + \frac{\mathrm{E}^2\mathrm{C}_0 \sin\theta}{mn\omega(d-a)^2\mathrm{D}}\right],$$

$$\mathrm{A}' = \frac{\mathrm{E}^2\mathrm{C}_0}{mn(d-a)^2}\left[1 - \frac{\cos\theta}{\mathrm{D}}\right],$$

$$\mathrm{B} = \frac{e\mathrm{EC}_0}{m(d-a)\mathrm{D}}.$$

The complete solution of the system of equations contained in (12) and (13) above can be obtained by well-known methods *, but, even without this, important information regarding the dynamical theory of the condenser-telephone can be derived from the equations as they stand. The above equations are, in fact, similar to those representing the disturbed motion of a series of masses, each mass being suspended from the mass preceding it in the series by a vertical spring, and the uppermost mass being similarly suspended from a fixed support To let this system correspond exactly with the condenser-telephone system described above, we have merely to suppose that the masses are all equal and that the springs are also all equal, and that the lowest or nth mass is operated on by forces represented by the K, A′, B terms shown in equation (13) in addition to the force applied to it by the spring connecting it to the mass above it. These forces evidently consist of a frictional resistance proportional to the velocity, a restoring force proportional to the displacement, and a disturbing periodic force. The motion of the condenser plates is therefore to be identified with that of a dynamical system whose general characteristics have been fully investigated elsewhere †.

* See, for instance, Rayleigh, 'Theory of Sound,' vol. i. chap. v.

† Lord Kelvin's 'Baltimore Lectures.'

For our particular purpose it is desirable first to form an estimate of the relative importance of the various terms appearing in the equations, such as the fundamental constant c^2 and the damping coefficient K. Probably the minimum value obtainable for the modulus Y would be that which corresponds with air as the dielectric material between the plates, namely, $1{\cdot}42\times10^6$ dynes per sq. cm. Taking A the area of each sheet as 6 sq. ft. or 5400 sq. cm., and d or $d-a$ as $\frac{2}{1000}$ inch or ·005 cm., and E as 200 volts, the values obtained are

$$\frac{YA}{d} = 1{\cdot}4\times10^{12} \text{ dynes per cm.:}$$

$$\frac{E^2C_0}{d^2} = 3\times10^9 \text{ dynes per cm.}$$

As we have chosen a minimum value for Y in forming this estimate, it appears that with any solid material as dielectric we may take $c^2 \doteqdot YA/md$, even with $E=500$ volts; and we may consider that the term containing A′ in equation (13) is small enough to be practically negligible in comparison with the terms retained, especially when n, the number of sheets, is any fairly large number. On page 504 of the earlier paper it is shown that the coefficient κ, which appears in the expression for K given in (13), has the value $A\rho_0V$, where ρ_0 represents the density of air, and V represents the velocity of sound in air. Taking the same value for A as before, we obtain as the value of κ, $2{\cdot}27\times10^5$. The remaining term in the expression for K can be estimated from the value just given for $\dfrac{E^2C_0}{(d-a)^2}$. From this it appears that K also is a small quantity compared with c^2. The resistance coefficient, moreover, has its maximum value near the frequency corresponding to electrical resonance and falls off rapidly to the steady value $\dfrac{\kappa}{2m}$ at the higher frequencies.

The motion of any one of the condenser plates represented by equations (12) and (13) above is evidently of the type

$$x_r = a_r \sin(\omega t - \theta - \epsilon_r),$$

where a_r and ϵ_r are constants. In this case the quantity with which we are specially concerned is the amplitude of the displacement of the outermost plate of the system

which transmits sound energy to the air. For a condenser consisting of two plates, the amplitude is given by

$$a_1 = \mathrm{B} \cdot \frac{1}{\sqrt{\{(c^2-\omega^2)^2+4\mathrm{K}^2\omega\}}} \quad . \quad . \quad . \quad . \quad (14)$$

For a condenser having three plates, $n=2$, the amplitude is given by

$$a_2 = \mathrm{B} \cdot \frac{(2c^2-\omega^2)}{\sqrt{\{(\omega^4-3c^2\omega^2+c^4)^2+4\mathrm{K}^2\omega^2(2c^2-\omega^2)^2\}}} \quad . \quad (15)$$

For $n=3$, we have

$$a_3 = \mathrm{B} \cdot \frac{(\omega^4-4c^2\omega^2+3c^4)}{\sqrt{\{(\omega^6-5c^2\omega^4+6c^4\omega^2-c^6)^2+4\mathrm{K}^2\omega^2(\omega^4-4c^2\omega^2+3c^4)^2\}}}, \quad . \quad . \quad . \quad (16)$$

and for the case of n free plates, we have

$$a_n = \mathrm{B} \cdot \frac{f(n, c, \omega)}{\sqrt{\{\mathrm{F}(n, c, \omega)\}^2+4\mathrm{K}^2\omega^2\{f(n, c, \omega)\}^2}}, \quad (17)$$

where F (n, c, ω) and $2\mathrm{K}\omega f(n, c, \omega)$ are the real and imaginary parts respectively of the determinant, ∇, obtained by eliminating all the variables but one from the equations of motion, and indicated below for the case of $n=4$:

$$\nabla = \begin{vmatrix} \mathrm{D}^2+2c^2, & -c^2, & & \\ -c^2, & \mathrm{D}^2+2c^2, & -c^2, & \\ & -c^2, & \mathrm{D}^2+2c^2, & -c^2, \\ & & -c^2, & \mathrm{D}^2+2\mathrm{KD}+c^2. \end{vmatrix} \quad . \quad (18)$$

In this the operator D is to be replaced by $i\omega$: and the A′ term is omitted as its effect on what follows is very small.

Equation (14), it will be seen, is in agreement with the corresponding result contained in equation (11) of the previous paper. In all cases the amplitude of the displacement of the outermost plate depends on the product of two factors, one being the amplitude of the forced vibration $\frac{e\mathrm{EC}_0}{m(d-a)\mathrm{D}}$ and the other, which we may denote by $\mathrm{F}(n)$, being a function whose value is determined by the elastic modulus of the dielectric material and by the number of sheets contained in the condenser. Neither factor becomes zero as the frequency

of the forced vibration $\omega/2\pi$ tends to zero. When $\omega=0$, the value of the amplitude is given by

$$a_n = \frac{e\mathrm{E}\mathrm{C}_0}{m(d-a)} \cdot \frac{n}{c^2}, \quad . \quad . \quad . \quad . \quad . \quad (19)$$

from which it appears that the amplitude at low frequencies increases directly as the number of sheets in the condenser.

The curve representing the amplitude of the nth plate for all values of the frequency, $\frac{\omega}{2\pi}$, has always one maximum or resonance point determined by the values of L, $n\mathrm{C}_0$, R, in the condenser circuit. This maximum occurs at the frequency $\frac{\omega}{2\pi} = \frac{1}{2\pi\sqrt{n\mathrm{C}_0\mathrm{L}}}$, and it is possible to choose conditions in the condenser circuit so as to make the amplitude curve either sharp or exceedingly flat in the neighbourhood of this maximum. This is illustrated by three curves representing the variation of $\frac{n\mathrm{C}_0}{\mathrm{D}}$ over the frequency range 0–1000, given in the earlier investigation, p. 506. In the case of a condenser having one free sheet only, a second maximum appears on the curve at the frequency corresponding to $\omega^2=c^2$, which we shall refer to as the standard mechanical frequency of the condenser. If the dielectric material be air, and if ·005 gram per sq. cm. be taken as a value of $\frac{m}{\mathrm{A}}$ for tinfoil sheets, and if d, the distance apart of the condenser sheets, be taken as one mil, the value of the standard mechanical frequency works out at about 50,000. From some results obtained for condensers with paper dielectric the value of the standard mechanical frequency in that case appears to be also in the neighbourhood of 50,000, which seems to indicate that the elastic resistance to compression of the dielectric is largely due to that of the air included between the plates. In the case of a condenser having n free sheets, the amplitude curve has n maxima in addition to the maximum corresponding to resonance in the condenser circuit. These maxima occur at frequencies given approximately by the values of ω determined by the roots of

$$\mathrm{F}(n, c, \omega) = 0 \quad . \quad . \quad . \quad . \quad . \quad . \quad (20)$$

In (17) these roots determine the frequencies of the free vibrations of the system under the supposition that the

frictional resistance term is negligible. The effect of the resistance term is, in general, to reduce the values of the frequencies of the free vibrations slightly below those given by (20), and, as our treatment is approximate, we may consider the values given by (20) as sufficiently near the true values for our purpose. The problem of determining the roots of equation (20) is one which has been solved in connexion with the analogous dynamical system of masses and springs referred to above (see Routh, 'Dynamics of a Particle,' § 305, p. 193). From this we obtain the result that the values of the frequencies corresponding to the free vibrations of the n plate condenser are given by

$$\frac{\omega_s}{2\pi} = \frac{c}{2\pi} \cdot 2 \sin \frac{2s+1}{2n+1} \cdot \frac{\pi}{2}, \quad . \quad . \quad . \quad . \quad (21)$$

where s may have any of the values 0, 1, 2, 3, ..., $n-1$. The lowest frequency of free vibration of the system is thus $\frac{c}{2\pi} \cdot 2 \sin \frac{\pi}{4n+2}$, and the highest is a little less than $\frac{c}{\pi}$. When n is moderately large the lowest frequency is $\frac{\pi}{2n+1}$ times the standard mechanical frequency, and the highest is almost twice the standard mechanical frequency. The amplitude curve has therefore n maxima in the range of frequency 0 to $\frac{c}{\pi}$, in addition to the maximum at resonance frequency for the condenser circuit. Since

$$2 \sin \frac{2s+1}{2n+1} \frac{\pi}{2} = 1, \quad . \quad . \quad . \quad . \quad . \quad (22)$$

when $s \doteqdot \frac{n}{3}$ approximately, we see that one-third of the total number of maxima occur at frequencies less than the standard mechanical frequency. At each of the successive maxima the value of the amplitude is given by

$$a_n = \frac{e\mathrm{E}C_0}{m(d-a)\mathrm{D}} \cdot \frac{1}{2\mathrm{K}\omega_s}, \quad . \quad . \quad . \quad . \quad (23)$$

this being $\frac{c^2}{2n\mathrm{K}\omega_s\mathrm{D}}$ times the amplitude corresponding to zero frequency.

From the solution which we have obtained above it would be possible to calculate the value of the intensity of sound

at any point of observation near a condenser telephone corresponding to any chosen frequency $\frac{\omega}{2\pi}$. The intensity of sound emitted at any frequency is directly proportional to the average amount of energy communicated to the air per unit of time by the upper plate of the condenser, a quantity which is to be found from the expression

$$W = \tfrac{1}{2}\rho_0 VA\omega^2 a_u^2. \quad . \quad . \quad . \quad . \quad . \quad (24)$$

The curve of intensity plotted against frequency has thus a series of maxima at the same frequencies as the maxima on the amplitude curve, but, as we see from (23), at these maxima we have $a_s a_n D = \text{const.}$, and the series of crests on the intensity curve all lie on a curve represented by

$$y = \tfrac{1}{2}\rho_0 VA \cdot \left\{\frac{eEC_0}{2Km(d-a)D}\right\}^2. \quad . \quad . \quad (25)$$

The intensity curve for the condenser-telephone accordingly passes through the origin and thereafter has a succession of maxima at gradually decreasing intervals over the range of frequency from 0 to $\frac{c}{\pi}$, and the crests of the curve all lie on the curve indicated by (25) above. Illustrations of the form of this curve are obtained by squaring the ordinates of the curves given in the earlier paper, p. 506.

The effect of increasing the number of sheets in a condenser is now readily followed. As each sheet is added the first maximum on the intensity curve passes toward lower and lower frequency values followed by the second and so on, while the curve itself rises more and more rapidly near the origin. In this way the response at the low frequencies continuously improves with increase in the number of sheets. Nevertheless, owing to the high value of the standard frequency, even when the number of sheets is very large only a few of the first maxima come within the audible range of frequency, so that the variations on the intensity curve within this range are very gradual. With the first maximum at frequency 1000, the second falls near frequency 3000, and so on. In the instruments which have proved most successful in transmitting speech and music, a large number of large sheets are employed, so that the first maximum corresponding to the longest free vibration, and the maximum corresponding to electrical resonance in the condenser circuit, are both well toward the low frequency end of the audible range. The sibilants are also satisfactorily

reproduced, with any desired range of low frequency sounds according to the number of sheets employed.

The above theory no doubt explains the fundamental dynamical theory of the condenser-telephone and indicates clearly the nature of the response curve and the conditions which determine the shape of the curve in any actual case. But it must be kept in mind that the conditions assumed in the analytical investigation do not represent closely the actual conditions of working of a condenser-telephone in practice. In neglecting all second-order terms we have restricted the investigation to the case where the e.m.f.'s impressed on the condenser are very small compared with the constant e.m.f. applied to its plates, whereas in some of the more important applications so far made of the condenser-telephone this condition is far from being fulfilled.

XII. *On the Specific Heat of Manganese Phosphide.*

By B. G. Whitmore, *B.Sc.* *

IT is well known that, on the Weiss theory of ferro-magnetism, an additional term appears in the specific heat of a ferro-magnetic body in the region of its magnetic critical temperature, owing to the loss of magnetic potential energy. This additional term is given by the expression $\frac{1}{2J} \cdot \frac{N}{\rho} \cdot \frac{dI^2}{dT}$, where N is the constant of the Weiss internal field, and ρ is the density of the material. Weiss † and his collaborators found that the specific heat varied in accordance with the above theory in the case of iron, nickel, cobalt, and magnetite. Sucksmith and Potter ‡ examined the behaviour of nickel and Heusler alloys by a much more accurate method than that used by Weiss, but their results showed considerable differences from those expected on the above theory. Recently, Bates § examined the behaviour of the specific heat of a substance consisting of equal parts of manganese and arsenic. From his experiments it was not decisively settled whether the large changes in the specific

* Communicated by Prof. A. W. Porter, F.R.S.

† Weiss and Beck, *Journ. de Physique*, vol. vii. p. 249 (1908); Weiss, Piccard and Carrard, *Arch. Sci. Phys. Nat.* vol. xlii. p. 378 (1916), & vol. xliii. pp. 113 & 199 (1917).

‡ Sucksmith and Potter, Roy. Soc. Proc. A, vol. cxii. p. 157 (1926).

§ Bates, Roy. Soc. Proc. A, vol. cxvii. p. 681 (1928).

heat in the neighbourhood of the magnetic critical point depended on dI^2/dT or upon dI/dT, *i.e.*, whether they were due to changes in internal magnetic energy, as Weiss supposed, or to a transformation with absorption of heat, from a magnetic to a non-magnetic state of the substance. The present experiments, which were suggested by Dr. L. F. Bates, were made to determine the behaviour of the specific heat of a ferro-magnetic material consisting of approximately equal parts of manganese and phosphorus.

The substance was prepared as described by Hilpert and Dieckmann *. Pure black amorphous manganese, obtained by distilling off the mercury from an amalgam produced by the electrolysis of a solution of manganese chloride, was heated with the correct amount of red phophorus in an evacuated and sealed quartz tube to a temperature of 600° C. for ten to twelve hours. The resulting substance was digested with hydrochloric acid for several days, washed, crushed, and dried. The composition of the material, which was kindly determined for us by Mr. H. Terry and Mr. Jahn, was very approximately 66 parts by weight of manganese to 34 of phosphorus.

The specific heat measurements were made by a modification of the Nernst method †. The finely powdered substance was packed in a light hollow copper cylinder, containing a heating coil of No. 42 S.W.G. double silk-covered manganin wire and a resistance thermometer coil of No. 44 S.W.G. double silk-covered platinum wire. Both wires were distributed as evenly as possible throughout the powder, and leads of No. 30 S.W.G. double silk-covered copper wire passed through small holes in a tightly-fitting copper lid. The calorimeter was suspended inside a brass vessel, the leads being taken out through a glass tube sealed in with wax. The brass vessel was evacuated by a two-stage Hyvac pump, and stood in an electrically heated and well stirred bath of water. The resistance of the platinum wire was measured by means of an excellent form of Callendar and Griffith's bridge, for the loan of which I am greatly indebted to Mr. N. Eumorfopoulos. The resistance was measured directly at a series of temperatures between 0° and 30° C., some water being placed inside the brass vessel to promote conduction. A table was then drawn up, giving the temperatures corresponding to each 0·1 ohm increase in resistance.

* Hilpert and Dieckmann, *Ber. der Chem. Gesell.* vol. xliv. p. 2831 (1911).

† *Cf.* Bates, *loc. cit.*

The temperature intervals were very nearly equal. To measure the specific heat at various temperatures a steady current, C, was passed through the manganin coil, and the times, t, at which the temperature of the resistance coil attained the above series of values, T, were noted. Then

$$(m.s+w)\,.\,\Delta T=\frac{C^2\,.\,R}{4{\cdot}18}\,.\,\Delta t,$$

where m is the mass of the phosphide, s its specific heat, w the thermal capacity of the copper cylinder and the coils, and R the resistance of the heating coil. If R and ΔT were constant, as was very nearly true, any variations in specific heat would be indicated by variations in Δt. The above statement neglects loss of heat by radiation, and this was eliminated by maintaining the water bath at a temperature equal to the average temperature of each given temperature interval during the whole of the time in which the calorimeter temperature traversed that interval. Several experiments were made over the range 0° to 35° C. The behaviour of Δt was almost linear, no very pronounced maximum being observed. A slight increase was observed at about 16° C., but the experimental arrangements did not permit this increase to be measured very accurately.

The variation of the saturation magnetic intensity was measured with a sample of the same powder. Two similar copper tubes were wound with coils of No. 36 double silk-covered copper wire, which were connected in opposition. These were mounted parallel to the lines of force in the field of a Du Bois electromagnet, and they were capable of rapid rotation through 180°. One tube was filled with the powder and the other left empty. The coils were connected to a ballistic galvanometer, and the deflexions observed on rotating the tubes were recorded. Since the field used was 1960 gauss, the substance was assumed to be saturated. The tubes were surrounded by an electrically heated bath of paraffin, and experiments were made at temperatures up to 45° C., where the ballistic throw became zero. The absolute value of the intensity of magnetization was found by comparing the ballistic deflexion when the coils were connected in opposition with that due to the coil wound on the empty tube alone, the dimensions of the narrow cylinder occupied by the substance being known. No trace of a temperature hysteresis, like that obtained by Bates in the case of the arsenide, was found.

Fig. 1 shows the variation of the ballistic throw or saturation intensity I with temperature, whilst in fig. 2 are plotted

both $\partial I/dT$ and $\partial I^2/\partial T$, together with the time intervals, Δt, which are a measure of the specific heat. It will be seen that the slight increase in specific heat does not exactly coincide with the maximum of either $\partial I/\partial T$ or $\partial I^2/\partial T$ in

Fig. 1.

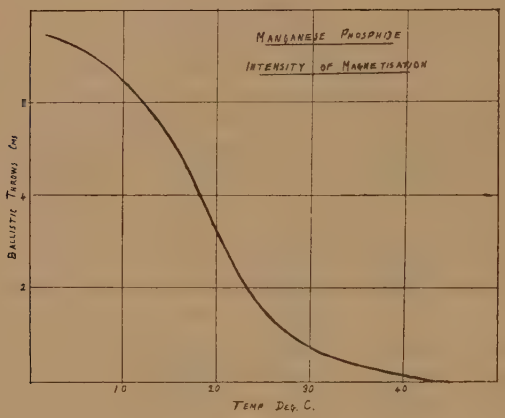
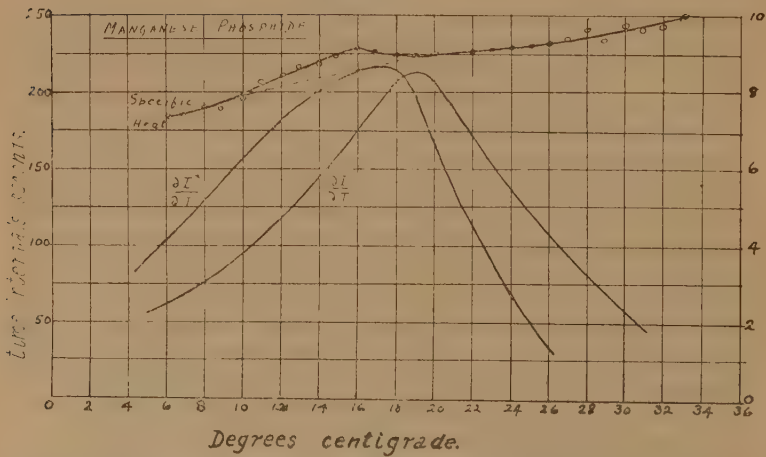


Fig. 2.



these experiments, but the general accuracy, in view of the small increase of specific heat observed, is not sufficient to enable us to state whether the difference is genuine or not. The maximum value of $\partial I/\partial T$ was 264 (e. m. u. per c.c.^{2}) per

degree C. We have no information of the value of N. It was hoped to measure the paramagnetic susceptibility of the substance at higher temperatures to obtain this information, but I have not had opportunity to do so. If the specific heat curve be carried straight across as indicated by the dotted line, and the increase above this be considered as due to the loss of magnetic energy, we may calculate the value of N required on the Weiss theory to account for this increase, as we know the value of $\partial I^2/\partial T$ approximately. Calculation shows that N must be about 1500. It therefore appears that the specific heat change is of the order predicted by the Weiss theory, though apparently it does not occur exactly at the expected temperature.

Summary.

Measurements were made on the variation of specific heat of manganese phosphide in the neighbourhood of its magnetic critical temperature. A small increase in specific heat, of the order expected on the Weiss theory, was observed near the temperature at which the value of $I.\partial I/\partial T$ was a maximum, though the accuracy of the experiment was insufficient to enable us to state whether the maximum value of the specific heat coincided with the maximum value of $I.\partial I/\partial T$ or with that of $\partial I/\partial T$.

I wish to thank Professor A. W. Porter, F.R.S., for the kind interest he has taken in this work, Dr. L. F. Bates for many helpful suggestions during its course, and the Department of Scientific and Industrial Research for a grant which enabled me to carry out the experiments.

Carey Foster Laboratory,
University College, London.

XIII. *The Action of X-Rays on Ferrous Sulphate Solutions.* *By* Hugo Fricke, *Ph.D.*, *and* Sterne Morse, *Department of Biophysics, Cleveland Clinic Foundation, Cleveland, Ohio* *.

X-RAYS have an action on aqueous solutions of ferrous sulphate which causes the iron to pass from the ferrous to the ferric state. The following investigation of this reaction was made in the course of a study of the

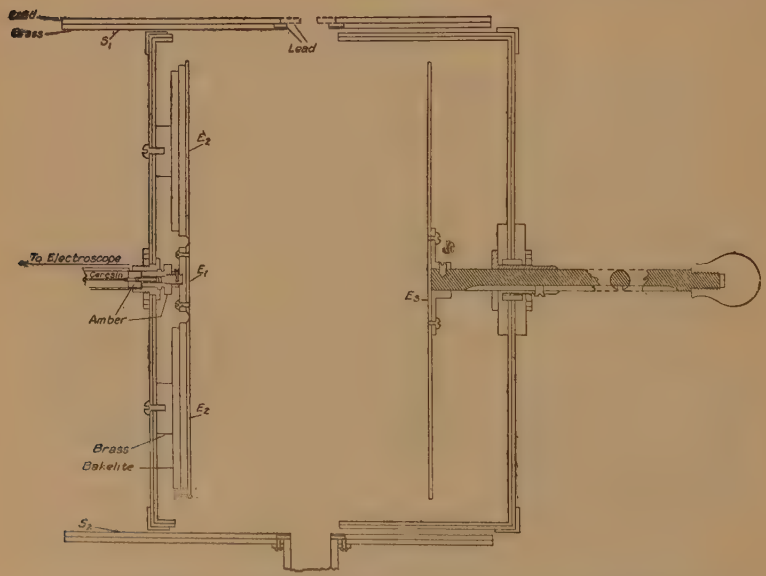
* Communicated by the Authors.

quantitative relationship existing between chemical effects and the ionization of a gas in its dependence on the wave-length of the Röntgen rays. A full account of this study will be reported later. Some of the results obtained have already been given at a recent meeting of the American Physical Society [1].

Experimental Technique.

The X-rays were produced with a water-cooled tungsten tube made of lithium glass, a transformer and mechanical

Fig. 1.



Large ionization chamber for measuring ionization in atmospheric air.

rectifier being employed. The potential was 100 K.V., the current 40 M.A.; the rays were filtered with a copper filter and a 1-mm. aluminium filter, the latter being added to absorb the characteristic rays from the copper ; the thickness of the copper filter varied in different experiments between 1/10 and 5/10 mm.

The intensity of the rays was determined by measuring the ionization produced by the rays in the chamber shown in fig. 1. The rays enter through the diaphragm in the slide S_1 and leave through the diaphragm in S_2.

The collecting electrode E_1 (4·98 × 20 cm.) is placed between the two guarding electrodes E_2 (11 × 20 cm.), the distance between E_1 and E_2 being ·35 mm. As the effective length of E_1 we take 5·02 cm. The wire connecting E_1 to the electrometer is placed inside a metal tube filled with ceresin. The electrode E_3 can move over 15 cm.; it is kept at such a potential as to make the electric force between E_1 and E_3 about 200 volts/cm., which is always found to be sufficient for saturation current. E_1 and E_2 are usually kept 7 cm. apart, a distance which is found to be sufficient for all irradiations to obtain the full ionization of the primary X-ray electrons. The ionization chamber is covered on the outside with 1 mm. lead except in the front, where 3 mm. is used. This is ample to protect the chamber against the small amount of stray radiation which is present in the room; when the diaphragm in the front of the chamber is closed, the electrometer does not show any observable discharge.

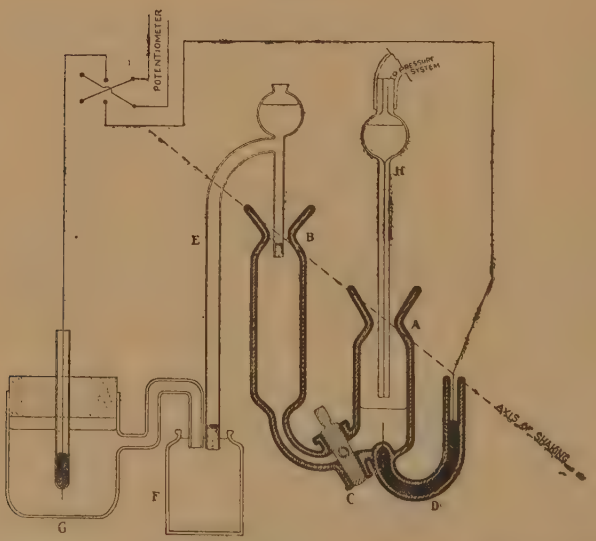
The ionization is determined by observing the time for the discharge of the electrometer over the length of its scale, which corresponds to a potential drop of 22·5 volts. The guarding electrodes E_2 are kept at the potential corresponding to the middle point of the scale; a change of six volts in the potential of E_2 changes the current to E_1 — about 1 per cent. when the electric force between E_1 and E_3 is 200 volts/cm.

The X-ray intensity at the front diaphragm is determined by dividing the observed ionization by the area of the front diaphragm and by the length of E_1 (5·02 cm.); diaphragms of different sizes (the diameters varying between 1/2 and 2 cm.) have been used, and it has been ascertained that the ionization current is proportional to the area of the diaphragm. All ionization measurements are corrected for variations in the density of the air due to variations in temperature and barometric pressure, air of 18° C. and 76 cm. pressure being taken as the standard reference.

As we shall see, the percentile amount of ferrous sulphate which is transformed increases in direct relation to the dilution of the solutions used. To obtain appreciable effects from the X-ray doses which it is practicable to apply, very high dilutions are required, the most dilute solutions used by us being 1/25,000 m. Furthermore, practical conditions of irradiation require that a very small amount of solution, about 1 or 2 c.c., be used. To meet these requirements, a special apparatus for electrometric titration was devised, a diagram of which is given in fig. 2. The solution to be

analysed is placed in the vessel A; this vessel, together with the connecting vessel B, are shaken through a few degrees at a rate of one or two hundred per minute. The axis of shaking is disposed diagonally and passes through the mouths of A and B, thus enabling the stationary capillary weight burette H and the connecting tube E to dip into the liquid in A and B. With these very dilute solutions no stable potentials can be obtained unless this shaking is done. B is separated from A by a stopcock C, which is so ground as to prevent the presence of any dead space in A. Owing

Fig. 2.



Apparatus for electrometric titration of ferrosulphate solutions.

to the difference in levels, any leakage through this stopcock, which is kept closed during a measurement, is towards the vessel A. The ends of E are closed by paper plugs through which slow leakage occurs from the bulb at the top of E. The comparison electrode G consists of a platinum wire which dips into a 1/10 n. solution of ferrous sulphate which is half oxidized. B, E, and F are all kept filled with a dilute solution of sulphuric acid of the same normality as that of the liquid in A and in G. It is evident that there is no possibility of any contamination of the content of either of the electrode vessels A and G by the content of the other. The solution used for

titrating is placed in the bulb of the capillary weight burette H, the capillary of which is about ·04 mm. in diameter and about 15 cm. long. The upper end of this burette is connected to a source of air-pressure, and by regulating it, the flow of the solution with which the titration is done can be regulated. For this capillary a pressure of 100 cm. of water causes about 1 c.c. to pass per hour. We have found the titration with sodium bichromate to be more practical than that with potassium permanganate.

The procedure of titration is as follows:—The ferrosulphate solution to be analysed is removed from the radiation cell by a bulb pipette each end of which is drawn into a capillary; and the filled pipette is weighed, its contents are emptied into A and it is re-weighed. A is shaken and the potential is measured. Somewhat more sodium bichromate is added than the amount necessary to oxidize the ferrosulphate completely, and A is again shaken. The potential rises to approximately plus 225 millivolts, and the shaking is continued until the potential remains constant. The weighed burette H containing a ferrosulphate solution is then put in place, the air-pressure being so adjusted that about 20 minutes is required for the back titration. Curiously enough, when ferrosulphate is added the potential again rises to a new maximum, where it remains fixed until just before the completion of the titration, when it begins to fall rapidly. The pressure is turned off and the titration finished with only the flow from the pipette, which is due to the hydrostatic pressure. At plus 150 millivolts the weight burette is rapidly removed, placed in the horizontal position, wiped dry, and again weighed.

In this investigation the ferrosulphate solutions contained 0·8 n. sulphuric acid prepared from Grasselli's best grade of acid. The water used was distilled from alkalin permanganate in pyrex glass, and its conductivity was controlled by a cell fused to the end of the condenser. This conductivity averaged $1–2 \times 10^{-6}$ ohms. Merck's Blue Label ferrosulphate was used. The titer of the bichromate solutions used was controlled by titration with a 1/10 n. solution of ferrosulphate, which was standardized with sodium oxalate. The bichromate used was re-crystallized from Baker's Analysed Grade. All normalities given were determined by weight of solution and not by volume.

The values for the ferrous ion concentration of the radiated solution as determined from the titration and from

the oxidation reduction potential of the solution agree very satisfactorily. Table I. gives the values obtained by the two methods for a 0·00100 n. solution. This good agreement shows that the radiated ferrous sulphate solutions do not contain any appreciable amount of substances other than the ferrous sulphate, which can be oxidized by sodium bichromate. We have chosen to use the values obtained

TABLE I.

Action of X-rays on ·00100 m. Ferrous Sulphate in ·8 n. Sulphuric Acid. A comparison of results obtained from titration oxidation, reduction potential of radiated solution.

Dose (arbitrary units).	Oxidation-reduction potential of radiated solution (millivolts).	Ferrous sulphate concentration in per cent. of original concentration from	
		Titration.	Potential.
7·1	−30·2	77·0	76·8
18·1	− 7·4	57·0	57·2
20·9	+19·0	31·7	31·9
27·5	+51·3	11·8	11·6
30·7	+70·0	7·0	5·8
36·7	+64·7	7·8	7·1
42·3	+80·3	5·2	3·8

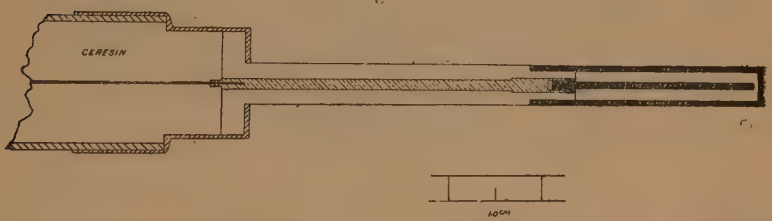
from the titration because they can be reproduced somewhat better than can the values obtained from the oxidation reduction potentials.

The cell in which the solution was kept during radiation was made of a plane piece of glass into which a hole was drilled. This was covered on both sides with thin cover glasses (·10 mm. thick). The cell was made air-tight by applying a small amount of melted vaseline along the edges of the cover glasses. Cells which varied in respect to area and thickness have been used.

The cell was usually placed about 20 cm. from the target of the X-ray tube, the width of the X-ray beam being regulated so as to be a few millimetres wider than the diameter of the cell.

The X-ray intensity during the irradiation of a cell was controlled by placing a specially constructed small ionization chamber directly beneath the cell. This chamber (fig. 3) consists of a graphite cylinder (wall thickness ·30 mm.) which is closed at one end, the other end fitting over an amber rod about 4 mm. in diameter; the inside length of the chamber is 2 cm., the inside diameter 3·5 mm. The wire connecting the electrode to the electrometer passes inside the amber rod and thereafter inside a metal tube filled with ceresin. The small chamber was for each type of radiation compared with the large air chamber described above. The principal reason for using the small chamber is that it will measure more accurately than the large chamber that part of the X-ray intensity which is due to the rays scattered by the irradiated liquid; this scattered intensity, however, never exceeds a small percentage of the total intensity.

Fig. 3.



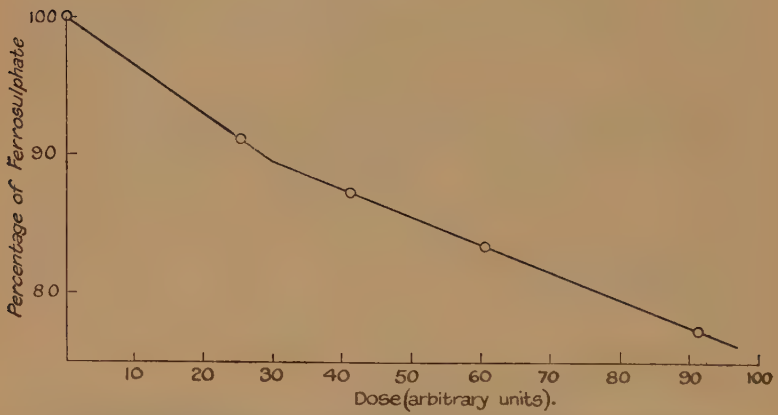
Small graphite ionization chamber.

The average X-ray intensity in the irradiated solution is obtained by multiplying by two correction factors the intensity recorded with the small chamber when the filled cell is in place. One is equal to the ratio of the X-ray intensities which are recorded when the small chamber is placed, first, at the point occupied by the centre of the cell and, secondly, in its normal position. (This differs from unity only by 1 or 2 per cent.) The absorption of the rays by the cell and by the solution is responsible for the second factor. In the present investigation the absorption of the filled cell was always so small (not exceeding 15 per cent.) that this factor, with sufficient accuracy, can be considered as equal to $\sqrt{\frac{I_2}{I_1}}$, I_1 and I_2 being the X-ray intensities recorded with and without the filled cell in place. The X-ray intensity is practically constant over the whole area of the cell.

Experimental Results.

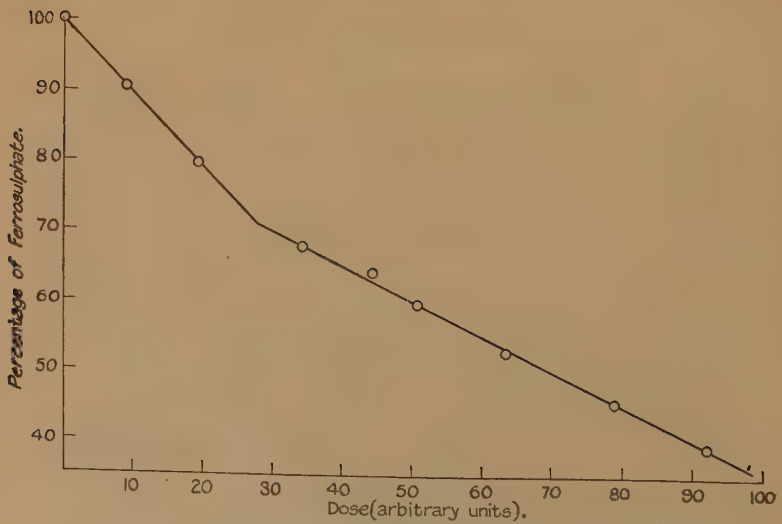
Various X-ray doses were used with various concentrations of ferrous sulphate ranging from $m/100$ to $m/25{,}000$. The

Fig. 4.



The action of different doses of X-rays on ·00878 m. ferrosulphate in ·8 n. sulphuric acid.

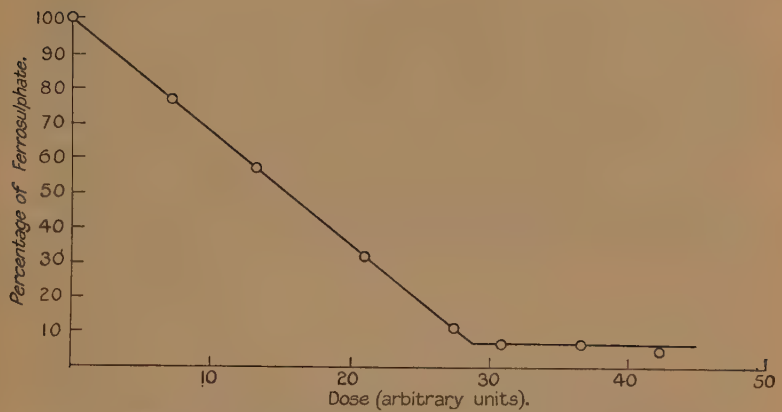
Fig. 5.



The action of different doses of X-rays on ·000337 m. ferrosulphate in ·8 n. sulphuric acid.

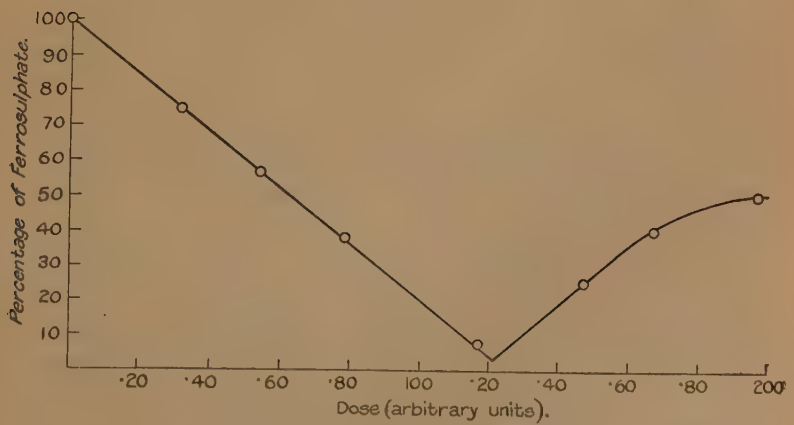
solutions were saturated with atmospheric air before irradiation and contained ·8 n. sulphuric acid. Representative results of these experiments are shown graphically in

Fig. 6.



The action of different doses of X-rays on ·00100 m. ferrosulphate in ·8 n. sulphuric acid.

Fig. 7.



The action of different doses of X-rays on ·0000406 m. ferrosulphate in ·8 n. sulphuric acid.

figs. 4–7, in which the X-ray dose is measured by the ionization produced in 1 c.c. of atmospheric air at 18° C. and 76 cm. pressure; the ionization is expressed in an arbitrary unit which is equal to 1800 electrostatic units.

For all solutions the graphs show an entirely linear relationship so long as a certain dose (29·0) is not exceeded, and within this range the absolute amount of ferrous sulphate transformed for a certain dose is independent of the concentration. Table I. gives, for each concentration used, the dose required within this range to change the concentration of the ferrous sulphate at the rate of one gram molecule in 1000 grams. When the value of the dose is in excess of 29·0, the relationship is again linear—at least as far as our measurements go, but the slope of the curve is here one-half of that present when the dose does not exceed 29·0. As we shall see presently, the number of molecules of ferrous sulphate transformed by the dose 29·0 is equal to the number of equivalents of gaseous oxygen dissolved in our solutions. This leads us to assume that the oxidation of the ferrous ions

Table II.

Dose required to change Concentration of Ferrous Sulphate Solutions 1 gram-molecule in 1000 grams.

Concentration (gram molecules in 1000 grams).	·00878	·00337	·00228	·00100	·0000406
Dose (electrostatic units).	$5{\cdot}5 \cdot 10^7$	$5{\cdot}2 \cdot 10^7$	$5{\cdot}5 \cdot 10^7$	$5{\cdot}5 \cdot 10^7$	$5{\cdot}5 \cdot 10$

is accomplished by a reduction of the gaseous oxygen of the solution, the complete consumption of the oxygen being indicated by the discontinuity in the reaction when the dose has a value of 29·0.

For ·8 n. sulphuric acid at 24° C., the approximate temperature at which our experiments were made, d, the Bunsen coefficient of absorption for oxygen, is 0·026 [2]. The barometer pressure was, during our experiments, about 74·5 cm., and consequently the volume of absorbed oxygen (taken at 0° C. and 76 cm. pressure) for 1 c.c. of our solutions is $\frac{\cdot 026 . 74{\cdot}5 . \cdot 21}{76} = \cdot 0054$ c.c.; the normality of this dissolved oxygen is $\frac{\cdot 0054 \cdot 4}{22{\cdot}4 . 1{\cdot}02} = \cdot 00094$ n., 1·02 being the specific density of ·8 n. sulphuric acid. Our arbitrary unit of dose equals 1800 electrostatic units, and the dose 29·0 therefore causes, according to Table II., the transformation

of $\frac{1800.29}{5{\cdot}5.10^7} = {\cdot}00095$ m. ferrous sulphate. This value agrees closely with the value for the normality of the dissolved oxygen.

It appears to us that the results given above can be accounted for only by assuming that the transformation of the ferrous ions is a secondary effect, due to activated water molecules which in turn are produced by the secondary X-ray electrons. A further justification for this assumption is found if one compares the number of ferrous ions which are transformed by the absorption of a certain amount of X-ray energy with the number of pairs of gaseous ions which are produced by the absorption of the same amount of X-ray energy in air, the numbers being, as we shall see, of the same order of magnitude.

The total true absorption of X-rays by a chemical element is the sum of the photo-electric absorption and of the absorption due to the production of recoil electrons ; the latter type of absorption we shall term the Compton absorption. Both are best expressed by stating the absorption of one gram electron of the substance and by defining the gram electron as the gram atom divided by the atomic number.

The chemical elements which for the most part are responsible for the X-ray absorption of atmospheric air and ·8 n. sulphuric acid respectively are so close to each other in the periodic table that no appreciable error can be introduced in the calculation of the ratio of their coefficients of absorption by assuming that the photo-electric absorption per gram electron varies as the third power of the atomic number, and that the Compton absorption per gram electron is independent of the atomic number. A calculation made in accordance with these assumptions shows that ·8 n. sulphuric acid and atmospheric air have the same coefficients of gram electron absorption.

One c.c. of atmospheric air at 18° C. and 76 cm. pressure contains $\frac{14{\cdot}45.273}{22400.291}$ gram electrons. One thousand grams of ·8 n. sulphuric acid contains 555 gram electrons. Therefore, when the same amount of X-ray energy is absorbed in the ferrous sulphate solution and in atmospheric air, and the dose does not exceed the value at which gaseous oxygen is completely consumed, the ratio of the number of ferrous ions transformed to the number of pairs of gaseous ions is $\frac{14{\cdot}45.273.2{\cdot}89.10^{14}}{555.22400.291.5{\cdot}5.10^7} = 5{\cdot}7$ (compare Table II.), the

accuracy of this figure being 2 per cent. If the solution does not contain oxygen, the ratio is $\frac{5{\cdot}7}{2} = 2{\cdot}8$. As we shall show in a later report, this ratio is independent of the wave-length of the rays, the range of wave-lengths investigated being ·20 to ·80 Å.U.

It is well known that by irradiation with X-rays or radio-active rays, pure water is transformed into hydrogen and oxygen. Duane and Scheuer [3] have determined the relation of this effect to the ionization in atmospheric air for the case of α-rays; they found that by complete absorption of α-rays in water and in atmospheric air, the ratio of the number of transformed water molecules to the number of pairs of gaseous ions is ·70. It is to be expected theoretically that this ratio will be the same for X-rays as for α-rays. We can therefore calculate the chemical effect obtained in our experiments in its relation to this effect on pure water; and we find that when a ferrous sulphate solution containing free oxygen is irradiated, $\frac{5{\cdot}7}{{\cdot}70} = 8{\cdot}2$ ferrous ions are transformed for every water molecule which is transformed when pure water is irradiated, the same amount of X-ray energy being absorbed in both cases. $\frac{8{\cdot}2}{4} = 2{\cdot}05$ oxygen molecules are reduced at the same time. If the ferrous sulphate solution does not contain free oxygen, the number of ferrous ions transformed is $\frac{8{\cdot}2}{2} = 4{\cdot}1$.

It will be seen from fig. 7 that when the action on the ·0000406 m. ferrous sulphate solution has reached a point at which nearly all the ferrous ions are oxidized, an apparent reversal of the reaction takes place, the curve representing this second stage of the reaction proceeding backwards with an initial slope which is numerically equal to the slope of the line representing the first stage of the reaction. The oxidation reduction potential of the radiated solutions rises continuously with increasing doses, until for the largest dose given (1·97 in our arbitrary unit) it reaches a value of plus 145 millivolts. Evidently, when the oxidation of the ferrous ions has reached its endpoint, an equivalent quantity of a substance (perhaps hydrogen peroxide) which is oxidized by sodium bichromate accumulates in the solution. We may recall that when pure water is irradiated, in addition to hydrogen and oxygen a small quantity of hydrogen peroxide

is formed. Since this substance is also destroyed by the radiation, the amount which can accumulate is limited, and it is possible that, in the dissociation of the water, hydrogen peroxide actually forms an intermediate compound. In order to obtain evidence as to whether or not the action of the X-rays on a ferrous sulphate solution may be due to a primary production of hydrogen peroxide, in a few experiments we have irradiated water or ·8 n. sulphuric acid with doses of the order of a fraction of one of our arbitrary units, and have then added the irradiated liquid to 1/4000 m. ferrous sulphate solution. The results were very irregular; as an average, effects were obtained which were about equal to the effects obtained by direct irradiation of a ferrous sulphate solution which does not contain free oxygen *.

The 0·00100 m. solution (fig. 6) does not show the apparent reversal of the reaction which we observe in the 0·0000406 m. solution. It is also noted that the X-rays do not cause a complete oxidation of the ferrous sulphate of this solution; but the reaction stops or at least proceeds very slowly when about 6 per cent. of the ferrous ions are left. A few measurements made with the stronger solutions, which are not included in the graphs, indicate that these behave in the same way. The oxidation reduction potential of the irradiated solution is apparently constant during this last stage of the reaction, the value being about 70 millivolts (see Table I.). The value of the ferrous ion concentration calculated from this potential agrees very well with the value obtained from the titration. Apparently X-rays are able to reduce the ferric ion; but it seems rather curious that the transition to the stationary part of the reaction should be as abrupt as our measurements indicate.

References.

(1) Fricke, H., "The Oxidation of Ferrous Sulphate in Aqueous Solutions by X-rays of different Wave-lengths: a determination of the Compton absorption," Phys. Rev. xxxi. p. 1117 (1928).

(2) Landolt-Börnstein, 'Physikalisch-Chemische Tabellen,' p. 770, (1923)

(3) Duane, W., and Scheuer, O., "Rescherches sur la décomposition de l'eau par les rayons α," *Le Radium*, x. p. 33 (1913).

* A few irradiations have also been made of a 1/1000 n. sodium bichromate solution; the sodium bichromate is reduced. We did not attempt to obtain any high degree of accuracy in these experiments; within the experimental accuracy of about 10 per cent. the effect expressed in equivalents is equal to the effect obtained for a ferrous sulphate solution which does not contain free oxygen.

XIV. *Adsorption at the Surface of Binary Liquid Mixtures.* *By* R. S. Bradley *.

ALTHOUGH the advantage of the impartial view that neither constituent of a binary mixture is to be regarded as the "solvent" has long been recognized, undue attention has been paid to the adsorption of one constituent without at the same time considering changes in the surface concentration of the other. Thus Rideal and Schofield † plot

$$\frac{d\sigma}{-\mathrm{RT}d\log a_1},$$

where σ is the surface tension of alcohol-water mixtures, a_1 the activity of the alcohol, and obtain a curve showing a maximum. In reality, however, they are not plotting the surface concentration of alcohol, but

$$\Gamma_1-\Gamma_2\frac{\mathrm{N}_1}{\mathrm{N}_2},$$

where Γ_1, Γ_2 are the Gibbs's surface excesses and N_1, N_2 the mol. fractions of alcohol and water respectively.

This is easily shown :

$$d\sigma=-\mathrm{RT}\Gamma_1\,d\log a_1-\mathrm{RT}\Gamma_2\,d\log a_2,$$

$$0=\mathrm{N}_1\,d\log a_1+\mathrm{N}_2\,d\log a.$$

Hence

$$\frac{-d\sigma}{\mathrm{RT}\,d\log a_1}=\Gamma_1-\Gamma_2\frac{\mathrm{N}_1}{\mathrm{N}_2}=\Gamma_1'.$$

In order to obtain Γ_1 and Γ_2, appeal must be made to some other relation, and this is given by the potential at the surface, as measured by Frumkin ‡. The range of the interfacial forces will be considered such as to confine adsorption to the surface layer.

Considering n molecules per cm.^{2} in the surface layer, these will form a condenser of thickness $d\cos\theta$, where

$$de=\mu,$$

e being the electronic charge, μ the electric moment of the

* Communicated by the Author.

† Rideal and Schofield, Proc. Roy. Soc. A, cxi. p. 57 (1925).

‡ Frumkin, *Zeit. Phys. Chem.* cxi. p. 190 (1924).

oriented molecule, θ the angle its axis makes with the normal to the surface. The charge per cm.^{2} is ne, so that

$$ne = \frac{V}{4\pi d\overline{\cos\theta}}, \quad \mu\overline{\cos\theta} = \frac{V}{4\pi n},$$

where V is the surface potential. The energy of 1 sq. cm. of the surface layer, when the thickness of the condenser is $d\cos\theta$, is

$$\frac{1}{2}\frac{V^2}{4\pi d\cos\theta},$$

the energy per dipole

$$\frac{V^2}{8\pi d\cos\theta n} = 2\pi n\mu e\cos\theta.$$

Hence, by applying the familiar theory of dielectrics *,

$$\mu\overline{\cos}\,\theta = \mu L(a),$$

where

$$a = \frac{2\pi n\mu e}{kT}$$

and $$L(a) = \coth a - \frac{1}{a}.$$

At the surface concentrations considered, the Langevin function becomes $1-\frac{1}{a}+2e^{-2a}\ldots$, so that, with sufficient accuracy,

$$\Sigma n_1\mu_1\left(1-\frac{kT}{2\pi e n_1\mu_1}\right) = \frac{V}{4\pi}.$$

If Γ_1, Γ_2 are the surface excesses in gm. mols. per cm.^{2} of alcohol and water at molar concentrations c_1 and c_2, we shall therefore have

$$\Gamma_1\mu_1+\Gamma_2\mu_2 = \frac{V}{4\pi N_0} - \mu_1 c_1^{\frac{3}{2}}10^{-2} - \mu_1 c_2^{\frac{3}{2}}10^{-2} + \frac{kT}{\pi e} + A,$$

where N_0 is Avogadro's number and A is a reference potential determined from the terminal condition on the alcohol side :

$$\frac{N_2}{N_1} = 0, \quad c_2 = 0, \quad V = 378 \text{ millivolts}, \quad n_1 = 7{\cdot}64.$$

The value for n_1 is calculated from the area 21·6 Å.U. for the head $-CH_2OH$ obtained from measurements on insoluble films.

* See, for example, Debye, 'Handbuch der Radiologie,' Band vi.

Values of Γ_1 and Γ_2 calculated from the equations above are given in Table I. For Γ_1', Γ_2' Rideal and Schofield's values have been used, while μ_1 has been taken to be $1{\cdot}6\ 10^{-18}$, $\mu_2\ 1{\cdot}7\ 10^{-18}$. Results are plotted in fig. 1: each curve shows a maximum.

Fig. 1.

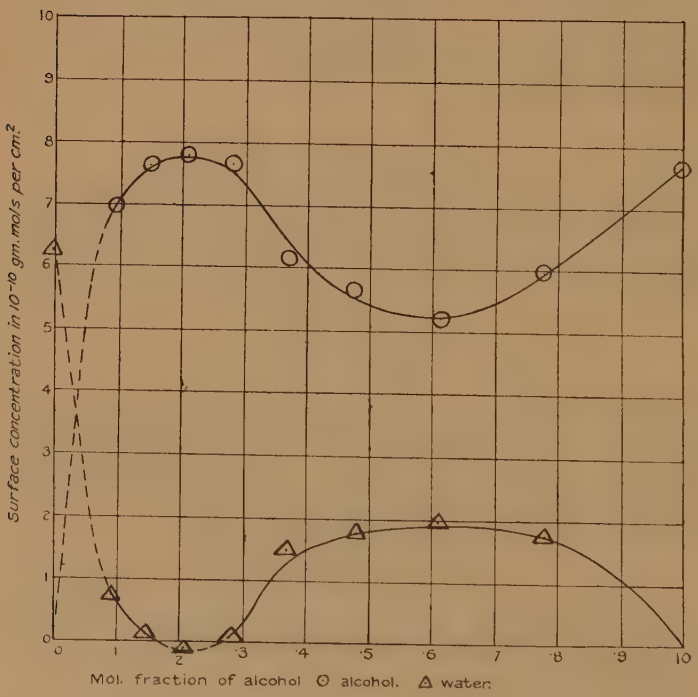


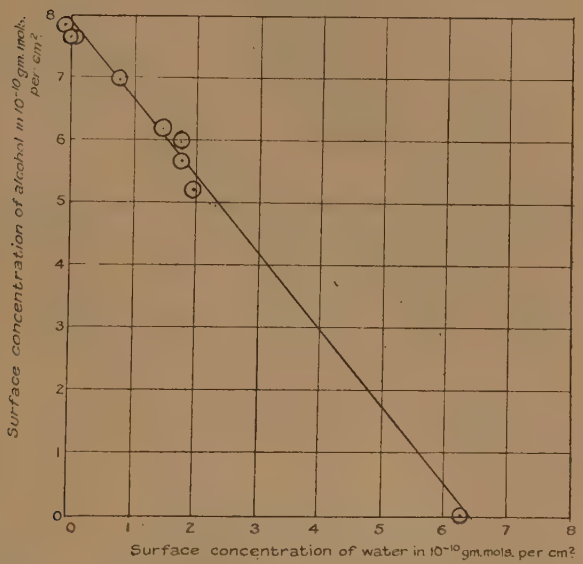
TABLE I.

N_1.	Γ_1.	Γ_2.	n_1.	n_2.
·778	1·83	— ·05	5·96	1·73
·611	1·31	— ·92	5·19	1·94
·477	2·00	—1·81	5·63	1·76
·370	2·80	—3·30	6·14	1·45
·281	4·62	—5·57	7·62	·04
·207	5·18	—6·58	7·78	—·15
·144	5·42	—7·11	7·60	·11
·089	5·28	—7·34	6·97	·75

The calculation may be checked by plotting n_1 against n_2. Simple replacement would require that

$$A_1 n_1 + A_2 n_2 = 1,$$

Fig. 2.



where $A_1 A_2$ are the sectional areas of oriented alcohol and water molecules. That this relation is roughly obeyed is seen from fig. 2, the straight line giving $A_2 = 25{\cdot}6$ Å.U.

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XV. *On the Magnetic Susceptibility of some Amalgams and Binary Alloys.* *By* W. G. Davies, *B.Sc.*, *and* E. S. Keeping, *D.I.C.**

§ 1. *Summary.*

THE relative magnetic susceptibilities of dilute amalgams of gold, tin, indium, and gallium with respect to that of mercury have been determined by means of a Curie-Chéneveau magnetic balance [1]. The (diamagnetic) susceptibility decreases in absolute value as the concentration of

* Communicated by Prof. E. J. Evans, D.Sc.

the dissolved metal increases, but not linearly. The effect per atom added on the susceptibility of mercury is greater for indium than for the other metals tried.

The susceptibilities of two series of binary alloys, copper-magnesium and copper-antimony, over a wide range of composition have also been determined. The susceptibility-composition curves for copper-magnesium show maxima corresponding to eutectics on the ordinary equilibrium diagram, and conspicuous minima corresponding to the known compounds $CuMg_2$ and Cu_2Mg. The equilibrium diagram for copper-antimony is more complicated, and two sets of experiments were carried out, one on the alloys prepared in the ordinary way and the other on specimens which had been carefully annealed. In all cases annealing increases the susceptibility, but the effect is very marked in the region from 20 to 60 per cent. of Cu. The only compound definitely indicated on the curve for the unannealed alloy is Cu_5Sb_2, but there is evidence of Cu_2Sb in the annealed alloy. This is the change of phase that would be expected, from the equilibrium diagram, to occur on annealing. Prominent maxima on the curves again correspond to eutectics formed.

§ 2. *Experimental Details.*

The Curie-Chéneveau magnetic balance may, with suitable precautions, be made to give very consistent readings [2], so that relative measurements of susceptibility can probably be relied on to 1 in 1000, although the absolute values are known much less accurately. In these experiments the standard substance used was pure mercury, the mass susceptibility of which was found, by direct comparison with water ($k = -0{\cdot}72 \times 10^{-6}$) to be $-0{\cdot}189 \times 10^{-6}$. This agrees well with Honda's value $-0{\cdot}19 \times 10^{-6}$.[3] Owing to the uncertainty about the absolute value, a round figure of $-0{\cdot}1900 \times 10^{-6}$ was adopted for the basis of comparison.

The same volume of amalgam was used in every experiment, the required weight being calculated from the density. The concentrations used were low enough (less than 0·6 per cent.) for the density to be calculated from the known proportion of the constituents. According to Morley and Muir [4] there is little or no volume change except for tin. The densities of tin amalgams of three different concentrations have been determined by Richards and Wilson [5], and the differences between experimental and calculated values are less than 1 in 1400. Moreover, a slight error in the

assumed density would produce a proportional error of the same sign in the observed deflexion, and as the ratio of deflexion to density determines, apart from minor corrections, the mass susceptibility, the effect on the calculated value of the latter would be negligible.

The most suitable suspension-wire was found, after various trials, to be phosphor-bronze, about 0·1 mm. in diameter. In the later experiments with alloys the great variations of susceptibility with composition made it necessary to use a stouter wire of platinoid (about 0·2 mm. in diameter). Careful inter-comparisons were made with the same substance on both wires. All observations were taken at room temperature. Great care was taken that the specimen under examination always occupied the same position relative to the field of the permanent magnet in the balance ; observations could then be repeated again and again with remarkable constancy, even though the specimen-tube had meanwhile been removed from the balance and replaced two or three times.

All the metals used for amalgams and alloys were the purest obtainable. The copper-magnesium alloys were prepared in the usual way and analysed electrolytically. For the susceptibility measurements they were powdered very finely in an agate mortar and introduced into the specimen-tube. Pure copper and magnesium were also examined. Finely-powdered copper was obtained by electrolysis of a copper nitrate solution under suitable conditions of current density. The densities of the various alloys were determined by means of a specific gravity bottle, benzene being used as the liquid for the Cu-Mg alloys, which are attacked by water. The masses used in each susceptibility measurement were calculated from the densities, the volume of metal being the same each time. Owing, however, to the difficulty of ensuring that the powder was always of the same degree of fineness, the apparent volume occupied by the powder in the tube possibly varied slightly. An experiment was carried out to determine the error due to this cause under extreme conditions, and it was found that the difference between the calculated susceptibilities for a very fine and a quite coarse powder amounted to 3 in 1000 ; it was estimated that the error under ordinary circumstances would be less than a quarter of this.

The copper-antimony alloys were chill-cast, and therefore formed of small crystals. Specimens were subsequently annealed at temperatures varying from 425° to 475° C. in an atmosphere of coal-gas. It has been shown by Emlyn

Stephens[6], working in this laboratory, that annealing has a marked effect on the electrical conductivity, thermo-electric height, and Hall coefficient for these alloys. Annealing was continued until it produced no further change in these properties. The compositions of the alloys were determined by dissolving them in concentrated hydrochloric acid and potassium chlorate, separating the antimony with ammonia and tartaric acid, and depositing the copper electrolytically. All the alloys were carefully tested for traces of iron, and rejected if any appeared.

§ 3. *Susceptibilities of Dilute Amalgams.*

Table I. gives the observed mass susceptibilities relative to mercury, for which k is taken as $-0{\cdot}1900\times10^{-6}$.

TABLE I.

Gold ($k=-0{\cdot}145\times10^{-6}$).			Tin ($k=0{\cdot}025\times10^{-6}$).		
Conc.	Temp. C.	$k\times10^6$	Conc.	Temp.	$k\times10^6$
0·0536	13·0	−0·1898	0·1654	15·0	−0·1900
0·0757	14·6	−0·1895	0·2475	15·0	−0·1899
0 1193	12·7	−0·1891	0·3230	14·5	−0·1887
0·1232	13·9	−0·1890	0·3465	14·5	−0·1885
0·1869	18·0	−0·1874	0·4064	14·8	−0·1879
0·2240	17·0	−0·1864	0·4548	14·4	−0·1877
0·2505	16·0	−0·1857	0·5712	14·8	−0·1877
Indium ($k=-0{\cdot}104\times10^{-6}$).			Gallium ($k=-0{\cdot}225\times10^{-6}$).		
0·0264	17·5	−0·1890	0·0326	18·0	−0·1897
0·0623	18·5	−0·1886	0·0810	19·6	−0·1888
0·1049	18·6	−0 1876	0·1298	16·6	−0·1878
0·1542	17·7	−0·1861	0·1817	18·4	−0·1873
0·2266	18·4	−0·1837	0·2436	18·9	−0·1870

The values quoted for the susceptibilities of the pure metals are mean values taken from Landolt-Börnstein. The concentrations are in percentages by weight. All these amalgams, like mercury, are diamagnetic, and the value of k may be supposed practically independent of the temperature. All four metals diminish in absolute value the diamagnetic susceptibility of mercury, indium being the most effective and tin the least. The effect of tin appears to be imperceptible up to a concentration of about 0·2 per cent. by weight.

The results are shown in the accompanying curves (fig. 1).

Fig. 1.

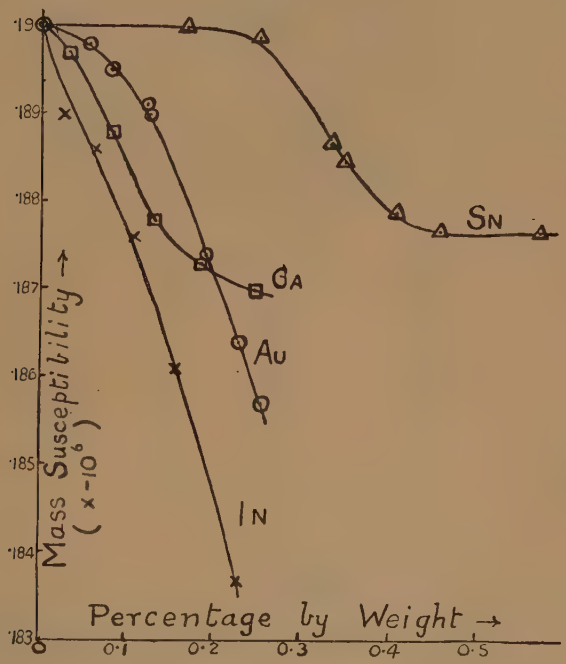


TABLE II.

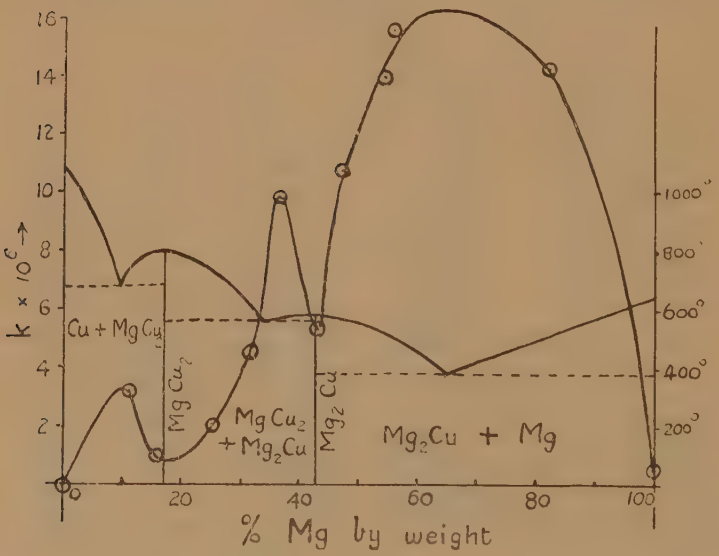
% Mg.	Density.	Temp. ° C.	$k \times 16^6$.	$k_{15} \times 10^6$.
0	8·93	22·4	−0·084	−0·084
11·0	6·64	16·3	$+3·17_2$	$+3·18_6$
15·7	5·69	17·0	$0·92_2$	$0·92_8$
25·1	5·47	18·7	$2·04_3$	$2·06_9$
31·6	4·62	18·9	$4·51_4$	$4·57_5$
36·4	3·90	17·5	$9·76_7$	$9·85_2$
43·0	3·58	17·4	$5·30_1$	$5·34_5$
47·1	3·18	17·1	$10·67_6$	$10·75_3$
54·2	2·98	18·9	$13·79_9$	$13·98_3$
55·6	2·50	15·8	$15·56_0$	$15·60_0$
82·2	2·25	17·5	$14·16_8$	$14·29_0$
100	1·74	17·8	0·559	0·564

§ 4. *Copper-Magnesium Alloys.*

All the alloys, as well as pure magnesium, were found to be paramagnetic, but copper itself is slightly diamagnetic. Table II. gives the observed susceptibilities for different compositions, and also the values corrected to a uniform temperature of 15° C. by Curie's law.

In fig. 2 the susceptibility curve for these alloys is drawn along with the equilibrium diagram [7]. It is evident that eutectics are marked by maxima on the susceptibility curve, and that the two well-marked minima on these curves correspond to the compounds $CuMg_2$ and Cu_2Mg.

Fig. 2.



§ 5. *Copper-Antimony Alloys.*

Table III. gives the results for both annealed and chill-cast specimens. Although both copper and antimony are diamagnetic, all the alloys are paramagnetic. The effect of annealing is in all cases to increase the susceptibility, sometimes more than fivefold.

The relation of the susceptibility curve to the equilibrium diagram [8] is shown in fig. 3. The equilibrium diagram is more complicated than for the Cu-Mg system, and the change of phase that accompanies the annealing of the alloys with

more than about 40 per cent. Cu is evident. The minima on the annealed and unannealed curves correspond respectively to compounds Cu_2Sb and Cu_5Sb_2, and there appears to be on the former curve an indication of the compound Cu_3Sb. Cu_2Sb is clearly the stable compound at the temperature of annealing. There is a very sharp maximum on both curves corresponding approximately to the eutectic at

TABLE III.

Unannealed Alloys.

% Cu.	Density.	Temp.° C.	$k\times10^6$.	$k\times10^6$.
0	6·62	22·8	−0·834	−0·834
20·5	7·15	17·4	+0·398	+0·401
29·9	7·58	17·7	0·709	+0·714
40·0	7·87	16·2	1·145	1·150
51·0	8·42	16·8	1·488	1·497
55·1	8·32	15·5	0·943	0·945
60·7	8·65	24·2	$4·04_9$	$4·17_8$
69·8	8·32	12·0	$13·97_1$	$13·82_6$
77·2	8·22	17·0	$10·05_2$	$10·11_9$
100	8·93	22·4	−0·084	−0·084

Annealed Alloys.

	Temp. of annealing.			
19·6		7·02	18·3	+0·582	+0·589
29·8	475°	7·45	17·8	$4·92_7$	$4·97_5$
41·5		7·86	17·0	$6·69_2$	$6·73_9$
51·0		8·46	20·2	$2·60_1$	$2·64_8$
55·5	425°	8·30	15·7	$4·59_3$	$4·61_0$
60·5		8·66	21·3	$5·44_5$	$5·56_1$
68·6	445°	8·34	12·5	$18·22_3$	$18·06_5$

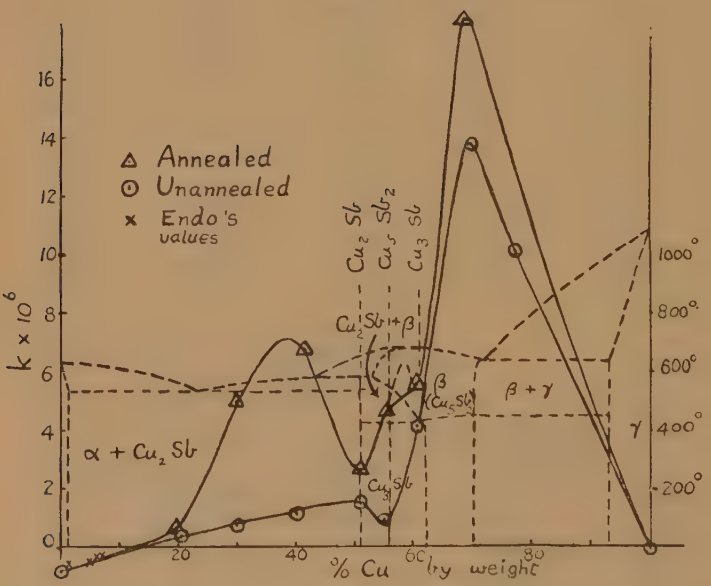
71 per cent. Cu, and no trace of the eutectic at 23 per cent. Cu. In the region where annealing produces a change of phase, there is a maximum on the annealed curve at about 40 per cent. Cu and one on the unannealed curve at about 50 per cent., but it is not evident from the diagram to what states of the alloy these maxima correspond.

The copper-antimony system has been examined also by Endo [9]. His tabulated values of the susceptibility relate only to alloys containing 0 to 7 per cent. Cu. These alloys are all diamagnetic, and the susceptibilities fit in fairly well

with our curve, as may be seen from the values plotted. Endo gives, however, a diagram in which there is apparently a linear increase of the mass susceptibility with concentration of Cu from $-0{\cdot}539 \times 10^{-6}$ at 1·4 per cent. to about $-0{\cdot}26 \times 10^{-6}$ at 50 per cent., although he does not adduce supporting data, and his values for 5, 6, and 7 per cent. Cu if plotted do not fall anywhere near this curve.

The susceptibilities of certain of the alloys investigated are remarkably high for this class of compound. One of

Fig. 3.



these (Cu-Sb, 68·6 per cent. Cu) was examined spectroscopically for traces of Fe, but no perceptible amount appeared to be present. The antimony used was stated by the firm supplying it to be 99·916 per cent. pure, the percentage of iron in it being 0·041. Since the value of the susceptibility of the antimony itself lies between those given in Landolt-Börnstein, it is evident that the presence of iron to this extent does not appreciably affect the susceptibility, and the spectroscopic examination indicates that no further iron was accidentally introduced during the process of manufacture of the alloy.

The observational work throughout has been carried out by one of us (W. G. Davies). We are deeply indebted to Prof. E. J. Evans for suggesting this research and for his continued interest.

References.

(1) Curie & Chéneveau, *J. de Phys.* ii. p. 796 (1903). Chéneveau & Jolley, Phil. Mag. xx. p. 357 (1910).
(2) Spencer & John, Proc. Roy. Soc. A, cxvi. p. 61 (1927).
(3) Landolt-Börnstein, p. 1202.
(4) Watts's Dictionary of Chemistry, i. p. 149.
(5) Richards & Wilson, *Z. phys. Chem.* lxxii. p. 141 (1910).
(6) Stephens, Univ. of Wales Thesis (to be published shortly).
(7) International Critical Tables, ii. p. 432.
(8) I. C. T. ii. p. 437.
(9) Endo, Tôhoku Univ. Sci. Reports, No. 14, p. 479 (1925).

University College of Swansea.

XVI. *The Influence of a High Potential Direct Current on the Conductivity of an Electrolyte.* *By* J. A. H. Leech-Porter, *M.Sc., and* T. Alty, *D.Sc., F.Inst.P., Professor of Physics, University of Saskatchewan, Canada* *.

THE conductivity of ordinary distilled water and of dilute solutions of electrolytes is found to vary between wide limits if a high potential direct current is passed through the solution. This variation was first noted in connexion with other work, but as the effects observed were very large and, so far as we have been able to find, have not already been described, the matter has been examined more fully.

Preliminary Experiments.

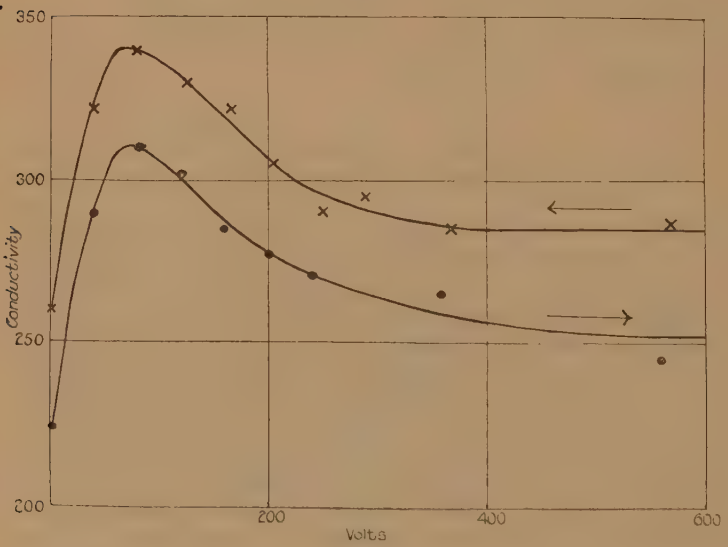
A cylindrical cell 7 cm. long and 2·5 cm. in diameter and having platinum end-pieces was filled with distilled water and the resistance between the end-pieces was measured. A potential of 240 volts was then applied between the platinum plates for some minutes, after which the resistance was again measured. Usually the application of the potential increased the conductivity by about 100 per cent. On stirring the water the original resistance was restored.

* Communicated by the Authors.

Variation of the Magnitude of the Resistance Change with Applied Voltage.

To investigate the change produced by different direct current voltages, the cell was filled with water and its resistance measured. A potential of 40 volts was then applied for ten minutes and the resistance was again measured, after which 80 volts was applied for ten minutes. This process was continued in steps of 40 volts until 600 volts in all had been applied to the cell, the resistance being measured ten minutes after each increase in voltage.

Fig. 1.



The cell was refilled with water and the experiment repeated, commencing with 600 volts, which was reduced in 40 volt steps to zero. The conductivity of the water was plotted against the applied voltage (fig. 1). In the graph the arrows indicate the order in which the points were obtained. It is seen that in the water used the change is greatest when 80 volts are applied, and that the change is independent of whether the voltage is increasing or decreasing. This independence seems to indicate that in this experiment an equilibrium state was reached between successive variations of the voltage, so that an interval between readings longer than ten minutes was not required.

In the above experiments the direct current used to produce the conductivity variations, and the alternating current used in the resistance measurements, were both applied to the same electrodes. It was therefore possible that the increased conductivity was an electrode effect. To guard against this possibility, the work was continued in a cell of different type. Two large plane electrodes were placed parallel to each other in a cylindrical glass vessel filled with a very dilute solution of HCl, and two small exploring electrodes could be introduced at any point between them. The direct current flowed between the large electrodes while the liquid resistance was measured between the small ones. In this way any possibility of the resistance change being due to the electrodes was eliminated. The resistance of the liquid at different points was measured before the D.C. was applied. After the latter had flowed for some minutes, the small electrodes were re-introduced and the measurements were repeated. It was invariably found that midway between the D.C. electrodes the resistance was very considerably greater than the normal, while close to the D.C. electrodes the resistance was greatly reduced. Stirring the water always restored the resistance to its normal value.

Further information was obtained by a slight modification of the above experiment. Two pairs of exploring electrodes, R_1 and R_2 (fig. 2), were kept in fixed positions and the D.C. was applied as before. The resistances across the electrodes R_1 and R_2 were measured every minute until steady values were reached. At this point the D.C. was reversed and the measurement of the resistances was continued until another pair of steady values was attained.

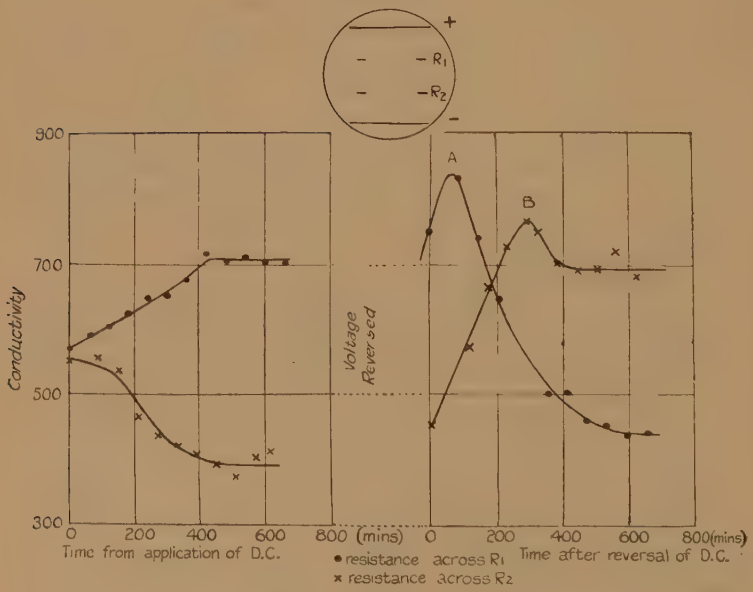
The arrangement of electrodes and the conductivity plotted against the time are shown in fig. 2. It will be seen that the resistance across one pair of electrodes increased while that across the other decreased. When the current was reversed, the resistances at R_1 and R_2 were interchanged. Also, on reversal, it will be noted that the conductivity at both pairs of electrodes first rises to a maximum and then falls to an equilibrium value. If the current be again reversed, this same effect is repeated.

It appears from these results that when the D.C. is applied ions of opposite sign are drawn out of the solution and collect near the two electrodes, so that an equilibrium state is set up in which the effect of diffusion is just balanced by that of the electric field. Since the conductivity of R_1 increased while that of R_2 decreased, in spite of the fact that the electrodes R_1 and R_2 were symmetrically placed with

respect to the D.C. electrodes, it appears that the ions near the negative D.C. plate are held closer to it than is the case at the other electrode. This difference may be due to differences between the coefficients of diffusion of the positive and negative ions.

When the D.C. is reversed the band of Cl^- ions collected near the positive electrode will move across the cell towards R_2. The peaks A and B on the curves seem to indicate that during this movement the ions remain more or less together. When the band moves through R_1 the conductivity there

Fig. 2.

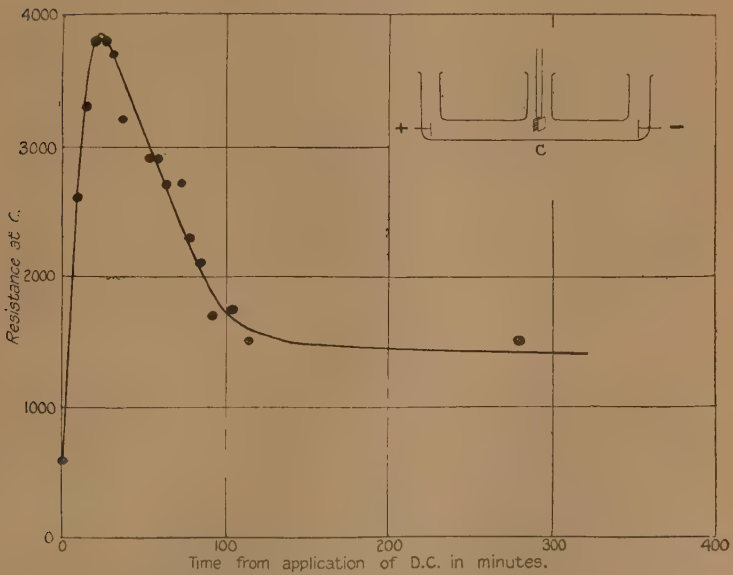


(A) is a maximum. When it arrives at R_2 the latter will show a similar maximum conductivity (B). Consequently the time between the occurrence of the two maxima A and B should on this view be the time required for the Cl^- ions to move from R_1 to R_2. The H^+ ions from the negative electrode do not show this band effect.

The above results indicated fairly clearly that in a very dilute solution of a salt the application of a strong potential has the effect of drawing a number of the ions from the central region of the liquid and concentrating them near the two electrodes. In these experiments the large D.C.

electrodes were of pure aluminium sheet. In order to ensure that the presence of the aluminium was not affecting the results the cell was replaced by one in which all the electrodes were of platinum. This cell consisted of a piece of 5 mm. bore glass tubing having a platinum electrode at each end. The distance between these electrodes was about 7 cm., and a pair of exploring electrodes could be introduced through an opening about midway between them. The exploring electrodes, when not actually in use, were kept in a separate container filled with some of the same solution as that in the experimental cell. They were introduced only

Fig. 3.



when a measurement of the liquid resistance midway between the D.C. electrodes was required. In this way any disturbing effect of the exploring electrodes on the distribution of the ions was avoided, and with this cell the results obtained were very consistent and reproducible. The potential was applied between the end electrodes and the resistance of the water midway between them was measured by means of the exploring electrodes and plotted against the time from the first application of the D.C.

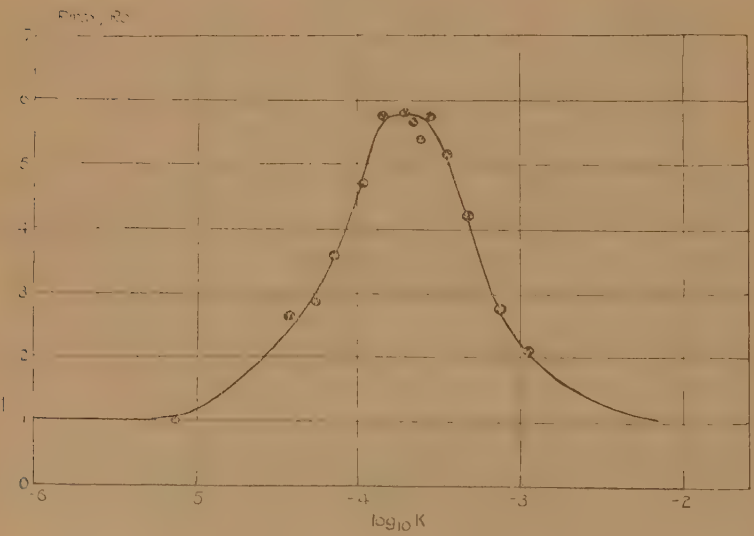
Fig. 3 is a typical graph obtained in this way. The resistance at C first rises to a sharp maximum and afterwards

falls off more slowly. This seems to show that the D.C. rapidly removes the ions from the central region, and that the conductivity in this region is only afterwards increased by the diffusion of the products of electrolysis from the end electrodes. It should be noted that in all these experiments the concentrations used are very small.

Variation of the Magnitude of the Resistance Change with the Initial Conductivity of the Solution.

The magnitude of the resistance change varies with the initial conductivity of the water. This variation was investigated with the cell above described. The electrolyte used

Fig. 4.



was a very dilute solution of HCl. For each value of the conductivity the graph of resistance-time for the exploring electrodes was obtained. The ratio of the maximum value of the resistance (R_{max}) to its original value (R_0) was then plotted against the logarithm of the specific conductivity (K).

The result is shown in fig. 4. For pure water, and for the more concentrated solutions of HCl, the resistance variation disappears. It rises to a maximum when the specific conductivity is about 2×10^{-4} ohm^{-1}. At this point the

maximum resistance midway between the D.C. electrodes is about six times its normal value.

The foregoing experiments indicate that the ions in a completely dissociated electrolytic solution may be collected in groups near the electrodes, leaving the liquid between them almost free from ions. Under these conditions there must be a space charge around each D.C. electrode, and the uniform potential distribution between the latter is entirely destroyed. This conclusion is easily demonstrated by the use of a potentiometer to measure the potential difference between different points in the liquid.

When the D.C. potential is reversed each group of ions moves across the cell to the opposite electrode, *in the form of a band*, *i. e.*, the ions do not spread out, but cross the cell in a single group. Experiment shows that the further the group travels the more diffuse it becomes, but, if the electric field is intense, diffusion plays only a secondary part, so that the movement of the group of ions can be easily observed. Rough measurements of the velocity of the ion band, taking into account the potential variations introduced, give a value of 74×10^{-5} cm./sec./volt/cm. for the mobility of the Cl^- ion. As no special precautions were taken to control the temperature, etc., this compares satisfactorily with the accepted value of 68×10^{-5} cm./sec./volt/cm. (Kaye & Laby, 'Tables,' p. 92.).

Summary.

The conductivity of very dilute electrolytic solutions is found to vary very greatly when the electrolyte is subjected to a high potential direct current. This variation occurs only in a limited range of conductivities and is absent when the conductivity of the solution is either too high or too low. It is most pronounced in the case of HCl solutions when the specific conductivity is about 2×10^{-4} ohm^{-1}, in which case the conductivity of the liquid may vary by as much as 600 per cent.

The results are explicable on the view that the high potential draws the ions from the centre portion of the liquid towards the electrodes, where they remain. If the direct current is reversed, each of these concentrated groups of ions moves across the experimental cell as a unit. It is suggested that the ionic mobility may be determined by this method.

XVII. *The Theory of Light-Scattering in Liquids.*

By Prof. C. V. Raman, *F.R.S.* *

IN the July, 1928 issue of the Philosophical Magazine, Dr. Y. Rocard has made certain comments on the paper by myself and Mr. Krishnan in the Phil. Mag. for March, 1928, to which it is necessary to reply.

The outstanding facts of observation in regard to scattering of light in liquids are that while the *intensity* of scattering at the ordinary temperatures is *much smaller* in liquids in proportion to the density of the fluid than in the corresponding vapour, the *depolarization* of the transversely scattered light is *much larger*. Any theory of light-scattering to be considered reasonably successful should not only explain these facts, but also indicate the manner in which the intensity and depolarization vary when the physical condition of the fluid is altered by change of temperature or pressure. The molecular theory of light-scattering outlined by me in 1922, and more fully formulated by Dr. Ramanathan in November of the same year and published early in 1923, had precisely the foregoing for its object, and in a general way it was confirmed by the series of experimental researches carried out at Calcutta on the scattering of light by vapours and liquids at high temperatures and pressures (Proc. Roy. Soc. A, cii. p. 151, 1922, and civ. p. 357, 1923). The purpose of the paper in the Phil. Mag. for March, 1928 by Mr. Krishnan and myself was to modify the original Raman-Ramanathan theory in the light of the newer knowledge concerning the molecular structure of liquids obtained by X-ray investigations. The fundamental idea of the paper is the use, instead of the spherically symmetrical polarization field of Lorentz, of an anisotropic polarization field, the constants of anisotropy depending mainly on the geometrical form of the molecules and also on the density of the fluid. The value of our attempt is to be judged not only by the greatly improved agreement between theory and the facts of observation thus brought about, but also by the success achieved with the aid of the same idea in explaining other electrical and optical properties of liquids which have hitherto been obscure (C. V. Raman and K. S. Krishnan, Proc. Roy. Soc. A, cxvii. pp. 1 and 589, 1927–28).

Dr. Rocard thinks that some of the conclusions set forth in the papers by Dr. Ramanathan and by ourselves had

* Communicated by the Author.

already been anticipated by Prof. L V. King. We believe that this remark has no adequate foundation. As a matter of fact, Prof. L. V. King never published any detailed theory of light-scattering in liquids. In a brief letter in 'Nature' (May 19, 1923) he put forward a conjectural amendment of the Raman-Ramanathan formula for the intensity of scattering. This was based on certain hypotheses regarding the origin of the observed depolarization in liquids, which were certainly inadmissible, as pointed out by me shortly afterwards in a letter to 'Nature' (August 4, 1923) to which no reply by Prof. King was ever published. Prof. King certainly did not contemplate the existence of the simple relationship between the observed depolarizations in liquid and vapour which forms an essential part in the Raman-Ramanathan theory; and to ascribe to him a formula for such relationship, as Dr. Rocard apparently wishes to do, would be quite unreasonable.

Dr. Rocard's note in the *Comptes Rendus* for August, 1925, to which he refers, did not contain any definite statement or proof that the polarization field within a liquid could be regarded as unaffected by the fluctuations of density, and indeed he now himself disclaims such belief. The grounds on which we, on the other hand (in agreement with Ramanathan) consider such assumption to be valid, appear to us to be of a quantitative nature. The weight of experimental evidence also seems to be in our favour.

210 Bowbazar Street, Calcutta.
August 2, 1928.

XVIII. *The Hall Effect and other Properties of the Copper-Antimony Series of Alloys.* *By* Emlyn Stephens, *M.Sc. (Wales), and* E. J. Evans, *D.Sc. (Lond.), University College of Swansea* *.

Introduction.

THE study of the variation of some electrical properties of alloys, in relation to the composition, has led to the conclusion that compounds formed of any two metals furnish singular points on a curve showing the relation between the electrical property and the composition of the alloy. This characteristic was discovered in the curve showing the relation between thermoelectric powers and concentration

* Communicated by the Authors.

of one metal in an alloy by Becquerel * and others, while Guertler † found the same result when examining the changes in the electrical conductivity and the temperature coefficient of electrical resistance, in relation to composition.

Smith ‡ has investigated, in addition to the phenomena already mentioned, the variations of the Hall and Nernst effects with the composition of alloys, and has observed similar singular points corresponding to compounds formed of the two metals.

The object of the present work is to obtain, for the purpose of comparison, experimental results showing the relation between the electrical resistivity, temperature coefficient of resistance, thermoelectric power, Hall coefficient, specific heat, and the composition of the copper-antimony series of alloys. These physical constants for a given alloy were in all cases determined by measurements on the same specimen.

The electrical properties of metals and alloys depend on their physical state. In the present experiments the values of the electrical resistivity and thermoelectric power were in the first place determined for the alloys after preparation, and were then redetermined for each alloy after annealing at a suitable temperature. The measurements were repeated until further annealing produced no change in these electrical properties. The temperature coefficient of resistance, specific heat, and the Hall coefficient in most cases were determined in the final state only. The Hall coefficients of Cu_2Sb and Cu_3Sb were also determined immediately after preparation of these alloys.

Kamensky §, from determinations of the electrical conductivities of the copper-antimony series of alloys, concludes that there are two compounds, Cu_2Sb and Cu_4Sb, while Baikous ‖, from the equilibrium diagram, considers that the compounds are represented by Cu_2Sb and Cu_3Sb.

Experimental Work.

The copper used for making the alloys was of electrolytic origin, while the antimony contained ·084 per cent. of impurities. The impurities were iron ·041 per cent., lead ·025 per cent., copper ·012 per cent., sulphur ·003 per cent., and arsenic ·003 per cent. The alloys were chill cast in an

* *Ann. de Chim. et Phys.* (4) viii. p. 408 (1866).
† *Zeits. für Anorg. Chem.* li. p. 397 (1906); liv. pp. 58–88 (1907).
‡ Phys. Rev. xxx. p. 178 (1911).
§ Phil. Mag. v. p. 270 (1884).
‖ Landolt & Börnstein, 3rd ed. p. 300.

iron mould in the form of plates. In considering the most suitable dimensions of the plates, attention was paid to the magnitudes of the determinations to be made. The Hall E.M.F. is usually a very small quantity, and as it varies inversely as the thickness of the plates, the latter were made as thin as possible. The great brittleness of some of the alloys prevented the preparation of satisfactory plates less than 0·4 cm. thick, and in all cases the mould was heated before pouring the alloy. The plates were approximately uniform, and the mean values of their dimensions, determined at regular intervals along them, were taken.

For these experiments ten plates were cast of the following percentage composition by weight:—(1) 80 per cent. Cu, 20 per cent. Sb; (2) 70 per cent. Cu, 30 per cent. Sb; (3) 66 per cent. Cu, 34 per cent. Sb; (4) 61·3 per cent. Cu, 38·7 per cent. Sb; (5) 55 per cent. Cu, 45 per cent. Sb; (6) 51·4 per cent. Cu, 48·6 per cent. Sb; (7) 40 per cent. Cu, 60 per cent. Sb; (8) 30 per cent. Cu, 70 per cent. Sb; (9) 20 per cent. Cu, 80 per cent. Sb; and (10) 100 per cent. Sb.

(1) *Electrical Resistivities and Temperature Coefficients of Resistance of the Alloys.*

The electrical resistivity was determined by fixing a plate of the alloy across two knife-edges, and determining the resistance of a known length by means of the Kelvin Bridge. The determinations were made at room temperature, which was measured by a thermometer placed in contact with the plate. The values of the resistivities in the initial and final states of the alloy are given in Table I. and Graph I.

TABLE I.

Composition of alloy by weight.	Resistivity before annealing, in microhms per cm.³	Temperature of plate in ° C.	Resistivity after annealing, in microhms per cm.³	Temperature of plate in ° C.
100 % Sb	40·9	16·0	—	—
80 % Sb 20 % Cu.	24·7	17·5	23·2	14·2
70 % Sb 30 % Cu.	18·1	17·2	17·2	14·3
60 % Sb 40 % Cu.	14·0	15·8	13·3	14·2
$SbCu_2$	11·0	15·2	11·0	13·5
45 % Sb 55 % Cu.	24·3	15·8	23·3	17·2
$SbCu_3$	77·7	18·0	99·1	15·8
34 % Sb 66 % Cu.	68·8	14·6	94·4	17·6
30 % Sb 70 % Cu.	84.0	14·1	90·1	13·8
20 % Sb 80 % Cu.	44·8	17·1	49·0	15·5
100 % Cu.	1·703	16·7	—	—

The mean temperature coefficient of resistance over the range of temperature between 0° C. and 100° C. was determined for each alloy in its final state, and these results are given in Table II. and Graph II.

Graph I.

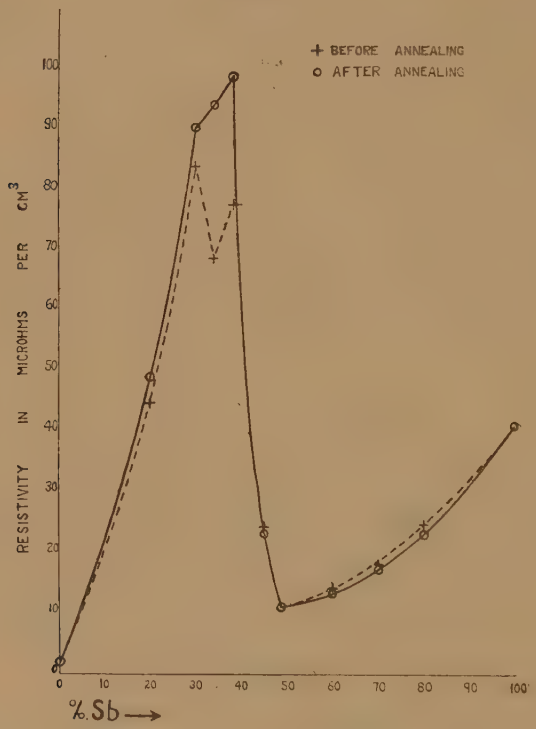


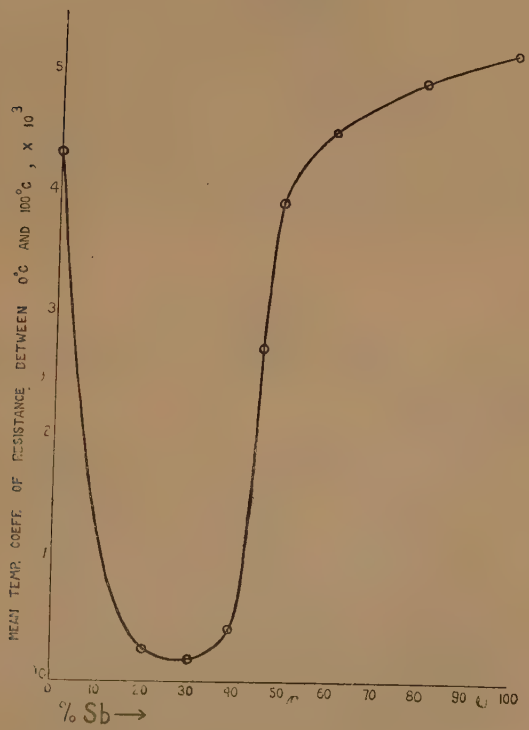
Table II.

Composition of alloy by weight.	Mean temp. coefficient of resistance between 0° C. and 100° C. $\times 10^4$.
100 % Sb	51·9
80 % Sb 20 % Cu ...	49·6
60 % Sb 40 % Cu ...	45·3
$SbCu_2$	39·6
45 % Sb 55 % Cu ...	27·4
$SbCu_3$	4·33
30 % Sb 70 % Cu ...	1·81
20 % Sb 80 % Cu ...	2·59
100 % Cu ...	43·5

(2) *Thermoelectric Power of the Alloys.*

The thermoelectric properties of the alloys were examined with copper leads soldered to the ends of the plates. The copper-alloy junctions were enclosed in two jackets, by means of which one junction could be kept at the temperature of steam and the other at the temperature of

GRAPH II.



running tap-water. The thermo-E.M.F. of the copper-alloy couples over this range of temperature was determined by means of a Tinsley vernier potentiometer. Repeated determinations of the thermoelectric power in micro-volts per degree centigrade when the temperature of the colder junction was varied over a range of several degrees agreed to 1 part in 500, so that the relation between E.M.F. and temperature was probably linear between room temperature and 100° C.

The thermoelectric power of copper with respect to lead was finally determined, and the thermoelectric power of the alloys in their initial and final states, with respect to lead, are given in Table III. and Graph III.

(3) *Hall Effect of the Alloys.*

The same method was employed for determining the Hall coefficient of the alloys as that fully described in an earlier paper by Miss P. Jones *, and therefore only a brief description will be given in this paper.

When a metal plate conveying an electric current is placed in a magnetic field, so that the lines of force are normal to the conducting plate and to the direction of flow of the electric current, a transverse galvanomagnetic potential difference is set up between the edges of the plate.

It has been proved experimentally that, for a given metal, the Hall P.D. denoted by E is given in abs. units by the formula

$$E = \frac{R.H.I.}{d},$$

where H is the magnetic field in gauss, I is the current in abs. units, d is the thickness of the plate in cm., and R is the Hall coefficient.

This coefficient R depends on the temperature, and, for some metals, on the intensity of the magnetic field as well.

It is of importance to note that the effect has different signs in various metals, and the convention with regard to sign can be readily understood by reference to fig. 1 (p. 168).

The rectangle X represents the plate, and the circle Y, with the arrowheads indicating the direction of the current in the electromagnet, represents the magnetic field. The direction of the primary current is given by E F, the position of the equipotential line before the application of the field by A B, and the position of this equipotential line when the field is applied by C D. If the equipotential line C D is rotated in the direction of the current in the electromagnet, the effect is said to be positive, and if the equipotential line is rotated in the opposite direction, the effect is said to be negative. The Hall effect in antimony and copper differ in sign, antimony giving a large positive effect and copper a low negative effect.

Although the Hall effect is very large for antimony, its values for the copper-antimony alloys vary in a marked

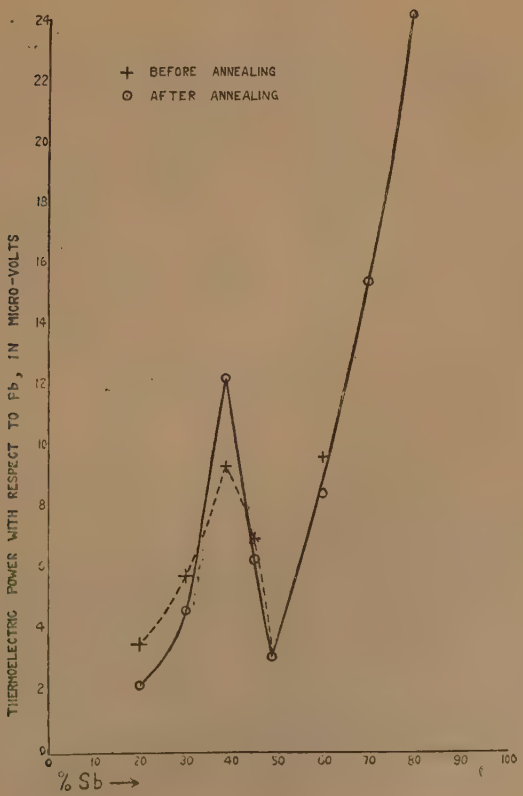
* Phil. Mag. (7) iv. p. 1312 (1927).

TABLE III.

Composition of alloy by weight.	Thermoelectric power with respect to Pb, in microvolts per degree centigrade. (Before annealing.)	Thermoelectric power with respect to Pb, in microvolts per degree centigrade. (After annealing.)
80 % Sb 20 % Cu ...	24·28	24·25
70 % Sb 30 % Cu ...	15·12	15·38
60 % Sb 40 % Cu ...	9·67	8·43
$SbCu_2$	3·09	3·07
45 % Sb 55 % Cu ...	6·98	6·30
$SbCu_3$	9·32	12·24
30 % Sb 70 % Cu ...	5·77	4·66
20 % Sb 80 % Cu ...	3·52	2·17

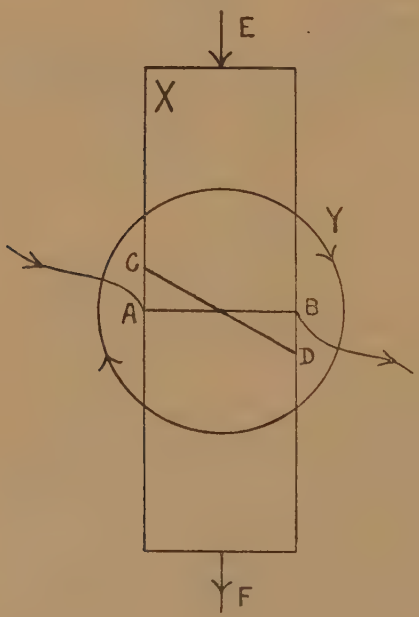
The direction of the thermoelectric force in all the alloys is such that the current flows from the alloy to the lead in the cold junction.

GRAPH III.



degree with the concentration of antimony in the alloy. The low value of the effect for some of the plates requires the use of a very sensitive galvanometer, and consequently a delicate Paschen galvanometer was used in the present experiments. It was mounted on a stone pillar, at a distance of $7\frac{1}{2}$ metres from a large circular electromagnet which had been rotated into such a position that its effect on the galvanometer was a minimum. This electromagnet excited by a current of 6 amperes produced a field of 8500 gauss in

Fig. 1.



the 1·5 cm. air-gap between the pole-pieces of circular section having a diameter of 9 cm.

The alloy plate under investigation was rigidly fixed in a vertical position in the magnetic field by two brass clamps which also served as leads for the primary current. These clamps were fixed to a wooden frame which also supported the secondary electrodes, consisting of spring copper contacts carried by bars of ebonite. These electrodes, which could be moved vertically along the edges of the plate by means of a screw arrangement, were connected to the galvanometer by long, well-insulated, flexible wires. These

wires were pulled taut so as to eliminate the effects of vibration as far as possible.

In a determination of the Hall coefficient the secondary electrodes were adjusted on the equipotential line AB (fig. 1). Then, with the secondary circuit closed, no deflexion is produced in the galvanometer when the primary current is reversed. On applying the magnetic field and again reversing the primary current, with the secondary circuit closed, a deflexion due to the Hall P.D. between the edges of the plate is produced in the galvanometer. The Hall P.D. was determined for several values of the magnetic field up to 8500 gauss, and a graph drawn showing the relation between the P.D. and magnetic field. The value of $\frac{E}{H}$ could be determined from this graph, and the Hall coefficient calculated from the equation:

$$R = \frac{E\,d}{H.I.}.$$

The maximum primary current (4 amps.) passing through the plate could be read on a Weston ammeter with an accuracy of about 1 in 1200, and the minimum current (1 ampere) used at the antimony end of the series with an accuracy of about 1 in 300. The magnetic fields corresponding to various currents passing through the electromagnet were determined by a search-coil and Grassot fluxmeter. The absolute value of the magnetic field when a current of 2 amperes passed through the magnet was determined by means of a delicate ballistic galvanometer and a search-coil of known mean area, and from this result corrections could be applied to the fields as determined by the fluxmeter. The magnetic field determinations are considered to be correct within about one-half per cent.

The Hall effect was determined at room temperature, the exact temperature being observed by an accurate thermometer suspended with its bulb in contact with the plate.

The experimental results * for the Hall coefficients are given in Table IV. and Graph VI.

It is, however, important to point out that in addition to the Hall potential difference a transverse galvanomagnetic temperature difference is set up between the edges of the

* Preliminary results on the Hall coefficients of some copper-antimony alloys in the unannealed state had already been obtained by Miss Phyllis Jones.

TABLE IV.

Composition of alloy by weight.	Thickness in cm.	Hall coefficient. before annealing.	Temp. of plate in ° C.	Hall coefficient after annealing.	Temp. of plate in ° C.
80 % Sb 20 % Cu.	·4192	—	—	+·0676	15·8
70 % Sb 30 % Cu.	·4140	—	—	+·0323	14·9
60 % Sb 40 % Cu.	·4087	—	—	+·0136	16·0
$SbCu_2$	·4140	+·00131	22·9	+·00130	21·7
45 % Sb 55 % Cu.	·4007	+·00143	21·2	+·00150	17·6
$SbCu_3$	·4166	+·00214	14·2	+·00176	14·9
30 % Sb 70 % Cu.	·4020	—	—	+·000111	18·1
20 % Sb 80 % Cu.	·4065	—	—	−·000324	22·8

GRAPH IV.

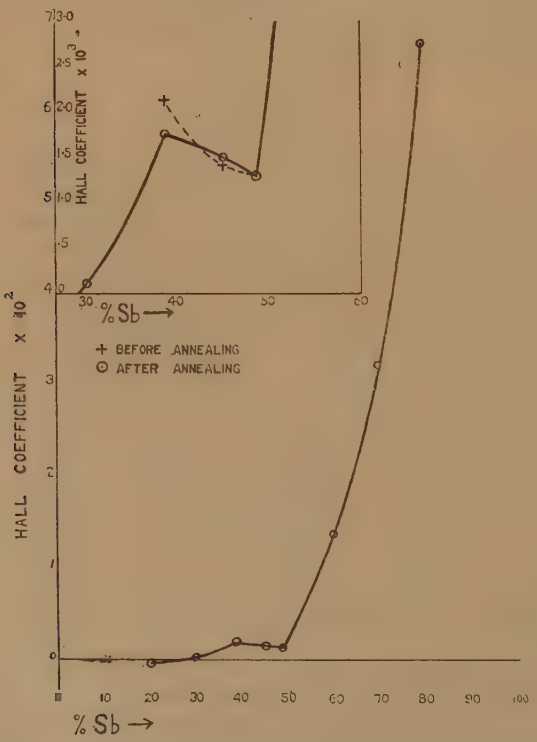


plate. This is the Ettingshausen effect and is usually very small. The difference of temperature, ΔT, is given by

$$\Delta T = \frac{P.H.I.}{d},$$

where H is the magnetic field in gauss, I the current in absolute units, d the thickness of the plate in cm., and P the Ettingshausen coefficient.

The Hall and Ettingshausen effects are superposed, and unless the secondary electrodes in the Hall-effect determinations are made of the same material as the plate itself, the Ettingshausen temperature difference ΔT set up between the edges of the plate will result in a thermo-E.M.F., $\theta . \Delta T$, in the secondary circuit, where θ is the thermoelectric power of the electrode with respect to the plate. Therefore the total potential difference as measured by the galvanometer in the Hall-effect determination is given by

$$E = E_H \pm \theta . \Delta T,$$

where E_H is the true Hall P.D.

Then R, the Hall coefficient becomes

$$R = \frac{E \times d}{H \times I} \pm P . \theta .$$

Generally the Ettingshausen coefficient P is very small, but the factor θ also determines whether a correction to the Hall coefficient is necessary. The secondary electrodes in the present experiments were made of copper, and some approximate determinations of $\theta . \Delta T$ were made for some of the plates.

Using constantan secondary electrodes soldered to the plate, the Ettingshausen thermo-E.M.F. was between 2 per cent. and 3 per cent. of the Hall P.D. With copper leads the Ettingshausen thermo-E.M.F. was too small to be observed with certainty, but computation from the values obtained for the deflexions due to the constantan leads showed that the Ettingshausen E.M.F. with the copper leads was less than ·5 per cent. of the Hall P.D. This is within the limits of experimental error (about 1 per cent.) of determinations of the Hall coefficients, and consequently no corrections have been made for the Ettingshausen effect in the present experiments.

(4) *The Specific Heats and Densities of the Alloys.*

The mean specific heats of the alloys between room temperature and 100° C. were determined by means of a Joly's steam calorimeter. The determinations were repeated several times for each alloy, and agreed to within 1 per cent. The results are given in Table V. and Graph V. The results

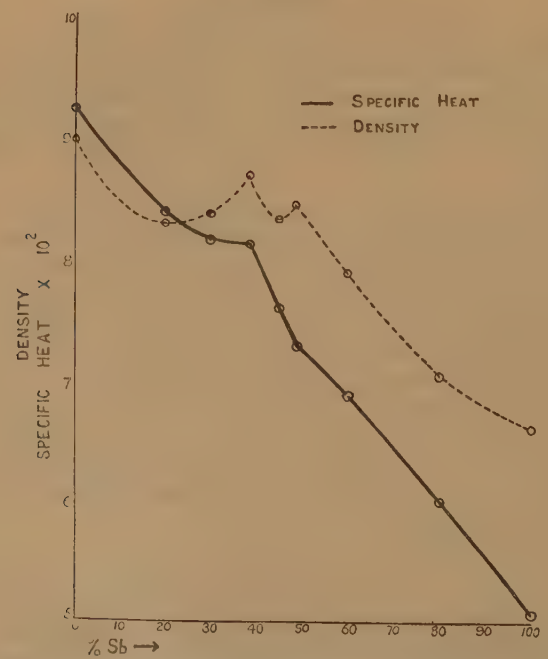
obtained by W. G. Davies* for the densities of the various alloys are also included in the same table and graph.

TABLE V.

Composition of alloy by weight.	Mean specific heat over the range of temperature indicated.	Density.
100 % Sb	·0506 (18·4° C.–100° C.)	6·62
80 % Sb 20 % Cu ...	·0599 (20·8° C.–100° C.)	7·02
60 % Sb 40 % Cu ...	·0687 (23·0° C.–100° C.)	7·86
$SbCu_2$	·0728 (21·6° C.–100° C.)	8·42
45 % Sb 55 % Cu ...	·0757 (18·9° C.–100° C.)	8·30
$SbCu_3$	·0809 (17·5° C.–100° C.)	8·66
30 % Sb 70 % Cu ...	·0812 (23·7° C.–100° C.)	8·34
20 % Sb 80 % Cu ...	·0835 (20·3° C.–100° C.)	8·26
100 % Cu ...	·0920 (19·1° C.–100° C.)	8·93

The specific heats of Cu_2Sb and Cu_3Sb have been determined by H. Schimpff† and P. Schübel‡, the values obtained by the former being ·0739 and ·0795 respectively.

GRAPH V.



* M.Sc. thesis on magnetic susceptibilities of amalgams and Cu–Mg and Cu Sb alloys.

† *Zeits. phys. Chem.* lxxi. p. 257 (1910).

‡ *Zeits. anorg. Chem.* lxxxvii. p. 81 (1914).

The Annealing of the Alloys.

The chill-cast alloys were annealed at temperatures obtained from the equilibrium diagram given in the International Critical Tables, vol. ii. The annealing was performed in an electric furnace, in an atmosphere of coal-gas to prevent oxidation. The alloys were heated to their annealing temperatures very slowly, and kept at these temperatures within a few degrees for a period of about 8 hours. Then the furnace was allowed to cool to room temperature before removing the alloy. The process was repeated several times for each alloy. The temperatures at which the various alloys were annealed are given below :—

20 per cent. Cu–80 per cent. Sb 30 „ „ Cu–70 „ „ Sb 40 „ „ Cu–60 „ „ Sb		475° C.
55 per cent. Cu_2Sb Cu–45 per cent. Sb 66 „ „ Cu_3Sb Cu–34 „ „ Sb		425° C.
70 per cent. Cu–30 per cent. Sb 80 „ „ Cu–20 „ „ Sb		445° C.

The annealing of one specimen was performed with the furnace evacuated to 1 mm. pressure, and the same results were obtained as for an alloy of the same composition annealed in coal-gas.

Discussion of Results.

The three curves showing the variation of the electrical resistivity, thermoelectric power, and Hall coefficient, with the concentration of Sb in the alloy, are similar in that they have singular points corresponding to both Cu_2Sb and Cu_3Sb, and the sign of the gradients of the curves is the same for corresponding compositions. While these curves are strikingly similar in form, they are in marked contrast to the curve obtained for the variation of temperature coefficient of resistance with the composition of the alloy. The curve for the temperature coefficient of resistance has no singular points corresponding to Cu_2Sb and Cu_3Sb, but shows a point of minimum temperature coefficient corresponding to an alloy of composition near Cu_4Sb.

The temperature coefficient of resistance of the alloys of composition between 100 per cent. Sb and Cu_2Sb diminishes

with the resistivity; but while the resistivity between Cu_2Sb and Cu_3Sb increases rapidly, so that the resistivity of Cu_3Sb is nine times that of Cu_2Sb, the temperature coefficient of resistance of Cu_3Sb is one-ninth that of Cu_2Sb.

The resistivity curve is not uniform between Cu_3Sb and 100 per cent. Cu, but shows a maximum value corresponding to Cu_3Sb and a sharp break corresponding to 70 per cent. Cu, 30 per cent. Sb. This irregularity at 70 per cent. Cu may be due to the hexagonal structure characteristic of Cu_3Sb extending as far as 70 per cent. Cu, 30 per cent. Sb, which nearly corresponds to Cu_4Sb.

The electrical conductivity of the copper-antimony series of alloys has been examined by N. Kurnakoff, P. Nabereznoff, and W. Ivanoff* over the range of temperature 10° C. to 600° C. While a sharply-defined maximum occurs on the isotherms of the electrical conductivity, corresponding to Cu_2Sb, no singular point is obtained corresponding to Cu_3Sb. The minimum temperature coefficient of electrical resistance, ·00014, obtained for a composition near Cu_4Sb, agrees closely with the values obtained in the present experiments, but the values of the temperature coefficients of resistance of Cu_2Sb and Cu_3Sb do not agree with the results of the present experiments. For the interval of temperature 25° C. to 100° C. the temperature coefficient of resistance of Cu_3Sb varies between the limits ·00022 and ·00112, while the coefficient for Cu_2Sb is ·00496, the corresponding values obtained in the present work being ·000433 and ·00396 respectively.

The Hall effect and thermoelectric power diminish in a similar manner as the composition of the alloy is changed from 100 per cent. Sb to Cu_2Sb. There is an increase in both effects between Cu_2Sb and Cu_3Sb, and singular points are obtained in both Curves III. and IV. corresponding to these compositions. In the range of composition between Cu_3Sb and 100 per cent. Cu the Hall effect and thermoelectric power again diminish, until corresponding to an alloy of composition 28 per cent. Sb, 72 per cent. Cu the Hall effect is zero, and changes sign with further addition of copper. Although the Hall effect for antimony is about 350 times that of copper and of opposite sign, the ratio of copper to antimony in an alloy giving zero Hall effect is as 72 : 28.

The Hall effect for pure antimony diminishes with

* 'Journal of the Russian Physico-Chemical Society,' Proceedings, pt. 2, xlviii. p. 701 (1916).

increasing magnetic field, but in the case of the copper-antimony alloys which were examined for magnetic fields up to 8500 gauss the Hall effect was found to be independent of the magnetic field for all the alloys, except the one of composition 80 per cent. Sb, 20 per cent. Cu. In this case there is possibly a slight decrease in the value of the Hall coefficient for high fields.

In Graph V., which shows the relations between the specific heat and density and percentage of antimony in the alloy, breaks occur corresponding to Cu_3Sb and Cu_2Sb, and apart from the region near Cu_3Sb, the specific heat would vary almost uniformly with the percentage of antimony in the alloy. The density curve also shows breaks corresponding to alloys of composition Cu_3Sb and Cu_2Sb.

In the present experiments annealing produced a very slight decrease in the resistivity of all the alloys of composition between Cu_2Sb and 100 per cent. Sb. In the range of composition Cu_3Sb to 100 per cent. Cu the alloys do not solidify into a single phase and a large increase in the resistivity is produced by annealing. In the chilled state the resistivity of Cu_3Sb was less than that of 70 per cent. Cu, 30 per cent. Sb, as determined by Kamensky *.

The effect of annealing on the thermoelectric power as shown in Graph III. follows no definite order. The resistivity and thermoelectric power of Cu_3Sb are both increased by annealing, while there is a diminution of 17 per cent. in the Hall coefficient. It is of interest to note that, in these experiments, annealing produced no appreciable variation in the resistivity, thermoelectric power, and Hall effect of Cu_2Sb.

Summary.

(1) The electrical resistivity, temperature coefficient of resistance, thermoelectric power, Hall effect, specific heat, and density of the copper-antimony series of alloys have been determined.

(2) The alloys were chill-cast in the form of plates, and the electrical resistivity and thermoelectric power were determined in this state. The resistivity and thermoelectric power were redetermined after the alloys were annealed at suitable temperatures, and the process of annealing was continued until the values of these electrical properties showed no further variation. The temperature coefficient of resistance, Hall effect, specific heat and density were then

* *Loc. cit.*

determined for the alloys in this final state. The Hall effects of Cu_2Sb and Cu_3Sb were also determined immediately after preparation.

(3) Singular points corresponding to both Cu_2Sb and Cu_3Sb are obtained in each of the curves showing the relation between electrical resistivity, thermoelectric power, Hall effect, specific heat, density, and the concentration of one metal in the alloy. No singular point and no evidence of the formation of compounds corresponding to Cu_2Sb and Cu_3Sb are obtained from the curve connecting the temperature coefficient of resistance and the percentage of antimony in the alloy.

(4) Annealing affected the electrical properties of the alloys to a degree depending upon their composition. Whereas the electrical properties of Cu_3Sb were greatly modified by annealing, those of Cu_2Sb remained practically unchanged.

The authors wish to thank Prof. C. A. Edwards, D.Sc., for his kindness in providing them with the materials used in this investigation, and facilities for the preparation of the alloys.

XIX. *The Analysis of Irregular Motions with Applications to the Energy-frequency Spectrum of Static and of Telegraph Signals.* *By* G. W. Kenrick, *Sc.D., Moore School of Electrical Engineering, University of Pennsylvania* *.

IN his well-known paper on "Selective Circuits and Static Interference," Carson † has emphasized that the energy-frequency spectrum of static and the required width of frequency band furnish ultimate and inherent limitations to the advantages to be gained by the use of linear selective circuits for the elimination of interference. In his analysis, Carson considers a function $R(\omega)$ measuring the energy of the interference on the frequency corresponding to ω $(=2\pi f)$. He assumes this function to be "a continuous finite function of ω which converges to zero at infinity and is everywhere positive . . . " but does not study in detail its form for various types of random disturbances.

It is the purpose of this paper to consider this energy-frequency distribution function $R(\omega)$ further, and to indicate

* Communicated by John R. Carson.

† 'Bell System Technical Journal,' April 1925.

a method by which its form may in certain cases be computed. The methods considered are of general application, but the specific examples chosen are suggested by the researches of Appleton and Watt *. These types of pulses disclose an $R(\omega)$ varying over a wide range directly with the square of the wave-length. This result is in general accord with the early observations of Austin and was also indicated by researches of Lord Rayleigh †, in which quite different types of random disturbances were considered. A similar result is found by Wiener for still other types of random motions‡, and it seems probable that it will be found to apply to the types of disturbances important in static. An exception is, of course, to be found in the case of inductive interference from power lines and other sources produced by man and having specific and well-defined frequency characteristics.

The frequency analysis of irregular motions has for some years engaged the attention of investigators §, and its exact solution produces many troublesome problems of rigour. The function which we have to consider, if experimentally determined, is defined over perhaps a very long but always finite interval of time T. The analysis of such a set of data, while it frequently furnishes results of engineering importance, represents, mathematically, an indeterminate problem by virtue of absence of data as to the behaviour of the function before the beginning or after the end of the interval of observation. Thus, any two wholly unrelated intervals of such data (represented in graphical form) may be placed end for end and a Fourier series development derived (in terms of the total interval thus produced) which will exactly reproduce the data periodically. The practical justification for considering a frequency spectrum of such a disturbance lies in the fact that the energy-frequency distribution over any important wide band of frequencies proves little or no different, if the total interval of data or any reasonably large fraction thereof is chosen and expanded into a Fourier series in terms of a fundamental period

* Appleton and Watt, "On the Nature of Atmospherics," Proc. Roy. Soc. A, ciii. pp. 95 and 96 (1923).

† Rayleigh, "On the Spectrum of an Irregular Disturbance," Phil. Mag. pp. 238–243 (1903); also Collected Works, v. pp. 98–102.

‡ Motion is used in this paper as a general term to denote any single valued real measurable function of a single independent variable (usually time).

§ See, for instance:—Arthur Schuster, "On Interference Phenomena," Phil. Mag. xxxvii. pp. 509–545 (June 1894), and "The Periodogram and its Optical Analogy," Proc. Roy. Soc. A, lxxxvii. pp. 136–140 (1906).

determined by its length. Each of these Fourier series developments would consist of series of terms of variable amplitudes and of frequencies equal to exact multiples of the arbitrarily chosen (and in no way inherent) base frequency, introducing the total time of observation available as one complete period. As the interval of observation grew long, however, a plot of amplitudes squared against frequency would lead to a series of lines * so closely spaced together as to give a well-defined and nearly invariable envelope. Since the exact position of the lines depends on the arbitrarily chosen fundamental period, we are inclined to associate more physical significance to the invariable envelope than to the actual lines. We choose our $R(\omega)$ curve so that the area under the curve is numerically approached by the sums of the squares of the coefficients of the terms of the Fourier development having frequencies in the same interval $\Delta\omega$. Students of probability theory will recognize this situation as exactly analogous to the representing of the probability of n events by a continuous function of n, in spite of the impossibility of the existence of a fractional number of events.

While the development in terms of a Fourier series expansion discloses the nature of the $R(\omega)$ curve, it is not always most convenient to arrive at $R(\omega)$ by Fourier series methods, and such methods are not adapted to the analysis of irregular motions not experimentally observed but defined over all time by known or assumed laws.

In this paper we shall introduce a formula derivable from the researches of Prof. N. Wiener †. By means of this formula it is possible to obtain a function $\theta(\omega)$, such that ‡

$$\theta(\omega) = \int_0^{\omega} R(\omega)d\omega. \quad . \quad . \quad . \quad . \quad (1\,a)$$

Moreover, when applied to a truly periodic function admitting a Fourier series development §, this function gives the sums of the squares of the amplitudes of the terms less than $\frac{\omega}{2\pi}$ in frequency.

Sharp lines or truly periodic disturbances of finite energy thus appear as perpendicular rises in this curve.

* For definition of lines, see page 180.

† See Appendix A.

‡ In cases where this integral exists.

§ The formula may, however, be applied to characterize a much more general class of functions than merely those periodic in the classical sense.

1. *Development of Fundamental Formulæ.*

Specifically, then, let us consider any function $y=f(t)$, defined either analytically or graphically over a very long (or infinite) time interval T. We will assume that the mean square value of this function over a sufficiently long period approaches a definite limit *, *i. e.*, that there exists a

$$\operatorname*{Lim}_{T\to\infty}\frac{1}{T}\int_0^T [f(t)]^2\,dt.$$

Subject to these conditions, a formula defining a function $\theta(\omega)$, having the relation to $R(\omega)$ noted in equation $(1a)$, may be shown to be†

$$\theta(\omega)=\frac{2}{\pi}\int_0^\infty \frac{\sin\omega u}{u}\,du\left[\operatorname*{Lim}_{K\to\infty}\frac{1}{K-u}\int_0^{K-u} f(t)f(t+u)\,dt\right]. \quad (1b)$$

While Prof. Wiener's investigations, on which the justification for this equation rests, are too extended to be summarized here, we will study some of the properties of the function $\theta(\omega)$ and show by direct computation that, when applied to a function admitting a classical Fourier series development, it leads to a function related to $R(\omega)$ in the manner described above. However, a development of the form considered by Prof. Wiener may be shown to be applicable to much more general types of functions than those admitting Fourier series developments.

The form of the graph $\theta(\omega)$ against ω $(=2\pi f)$ for a function having predominantly but not entirely random characteristics is shown in fig. 1.

Several things may be noted in regard to this function, *i. e.* :—

(1) It is monatonic, *i. e.*, it rises continuously or, at least, it never decreases.

(2) The rise between any two ω's is proportional to the energy in the spectrum of $f(t)$ over that region.

* Certain other closely allied conditions are assumed, but will in most practical cases be found to exist in practice, provided we limit ourselves to functions which are nowhere infinite and possess but a finite number of finite discontinuities in a finite range.

If we also introduce the condition of periodicity, *i. e.*, that there exists a quantity p, such that for all values of t, $f(t+p)=f(t)$, our function becomes periodic in the classical sense. Our analysis applies to such functions but also to many not satisfying this condition.

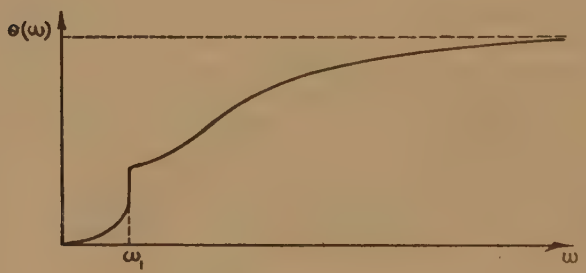
For a complete discussion of mathematical rigour, see references given in Appendix A of this paper.

† See Appendix A.

(3) Whenever there is a "line" in the $f(t)$ spectrum there is a sharp rise in $\theta(\omega)$, as shown at ω_1 in fig. 1. Thus we may define analytically the line components in a function not admitting a Fourier series development as that series of sinusoidal terms which, when subtracted from $f(t)$, will yield the same $\theta(\omega)$, except at that set of points at which vertical rises in $\theta(\omega)$ occur, and at these points produce a continuous $\theta(\omega)$. In practice it is never possible by the use of a finite interval of data to differentiate conclusively between merely a narrow region of rapid rise and a region in which a vertical rise occurs.

$\theta(\omega)$ is computed with the aid of a second function which is itself of no inconsiderable interest and importance. This function, which we term $\phi(u)$, represents the correlation of the original function $f(t)$ with itself under a displacement u

Fig. 1



and is the function inside the square brackets in equation (1), *i. e.*,

$$\phi(u) = \operatorname*{Lim}_{K \to \infty} \frac{1}{K-u} \int_0^{K-u} f(t) f(t+u)\, dt. \quad . \quad . \quad (2)$$

Where $f(t)$ represents the original function under investigation, K is the total observed interval, and u is a parameter.

In the case of graphical data, the correlation function $\phi(u)$ may be fairly readily computed by mechanical means. A typical correlation curve of a function of predominantly but not wholly random characteristics is shown in fig. 2.

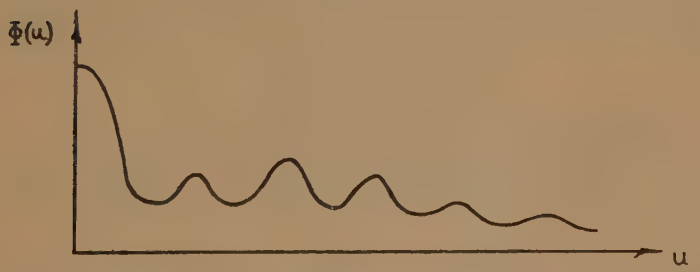
While this correlation function $\phi(u)$ is a necessity in further computations, its general form furnishes in itself considerable information of value to the investigator. Thus, we shall see presently that a "line" component in $f(t)$ leads to a $\phi(u)$ component which is sinusoidal, and hence does not decrease (except periodically) with increasing u.

The rapidity with which the correlation function $\phi(u)$ falls off with increasing u may, then, be used as a measure of the importance of disturbances not due to line components in the phenomenon under consideration.

2. *The Correlation Function $\phi(u)$ for the Special Case of a Function admitting a Fourier Series Development.*

We will now illustrate the use of the formula by applying it to a function admitting a Fourier series development. This will also serve to show the relation between $\phi(u)$ and the sums of the squares of the coefficients in this case. In applying formula (1 *b*) we have first to evaluate the quantity in brackets, which is simply the important $\phi(u)$ function already mentioned on page 180 (equation 2), *et seq.*

Fig. 2.



Thus, if we have a function $f(y)$ defined by the Fourier series,

$$f(y) = \sum_{n=1}^{n=\infty} a_n \sin(2\pi n y + \theta_n), \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

we have

$$\phi(u) = \operatorname*{Lim}_{K\to\infty} \frac{1}{K-u} \int_0^{K-u} \left[\sum_1^\infty a_n \sin(2\pi n y + \theta_n)\right] \times \left[\sum_1^\infty a_m \sin 2\pi m(y+u) + \theta_m\right] dy, \quad . \quad . \quad (4)$$

$$\phi(u) = \operatorname*{Lim}_{K\to\infty} \frac{1}{K-u} \int_0^{K-u} \left[\sum_1^\infty a_n (\sin 2\pi n y \cos\theta_n + \cos 2\pi n y \sin\theta_n)\right] \times \left\{\sum_1^\infty a_m (\sin 2\pi m(y+u)\cos\theta_m + \cos 2\pi m(y+u)\sin\theta_m)\right\} dy. \quad . \quad . \quad . \quad . \quad . \quad . \quad (5)$$

Further use of the formulæ for $\sin(a+b)$ and $\cos(a+b)$ enables us to reduce this to

$$\phi(u) = \tfrac{1}{2}\sum_{n=1}^{n=\infty} a_n^2 \cos 2\pi n u. \quad . \quad . \quad . \quad . \quad (6)$$

Thus, we see that in obtaining $\phi(u)$ we have already evaluated the sums of the squares of the coefficients in the Fourier series, each multiplied by $\frac{1}{2}\cos 2\pi n u$. Phase differences have, moreover, been eliminated.

An interesting feature of the $\phi(u)$ curve corresponding to a "line" spectrum is its non-decreasing character, *i. e.*, its definite mean square value over an indefinitely large interval of u. A $\phi(u)$ decreasing rapidly toward zero with increasing u definitely indicates the absence of any important line components in the given function.

To verify formula (1 *b*) for $\theta(\omega)$ for this case of a Fourier series we have now merely to use equation (1 *b*), written in the form

$$\theta(\omega) = \frac{2}{\pi}\int_0^\infty \frac{\sin \omega u}{u}[\phi(u)]du. \quad . \quad . \quad . \quad (7)$$

Substituting equation (6) in (7), we have

$$\theta(\omega) = \frac{2}{\pi}\int_0^\infty \tfrac{1}{2}\sum_1^\infty \frac{a_n^2 \cos 2\pi n u \sin \omega u}{u}\,du \quad . \quad . \quad . \quad . \quad . \quad . \quad (8)$$

or

$$\theta(\omega) = \frac{1}{\pi}\int_0^\infty \left(\sum_1^\infty \frac{a_n^2\{\sin(\omega+2\pi n)u + \sin(\omega-2\pi n)u\}}{2u}\,du. \quad (9)\right.$$

It is well known that *

$$\frac{2}{\pi}\int_0^\infty \frac{\sin Ku}{u}\,du = \left\{\begin{array}{ll} 1 & \omega>0 \\ 0 & \omega=0 \\ -1 & \omega<0 \end{array}\right\}. \quad . \quad . \quad (10)$$

Hence

$$\theta(\omega) = \tfrac{1}{2}\sum_{s=1}^{s=n} a_s^2, \quad . \quad . \quad . \quad . \quad . \quad (11)$$

where

$$n < \frac{\omega}{2\pi} < n+1.$$

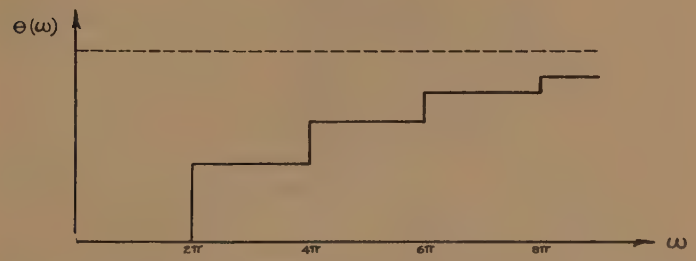
Thus it will be observed that in the case of a Fourier series the quantity $\theta(\omega)$ measures the sums of the squares of the amplitudes of the frequency components up to the frequency $\frac{\omega}{2\pi}$.

* See, for instance, Wilson's 'Advanced Calculus,' p. 366.

A typical plot of $\theta(\omega)$ for a function which admits of a Fourier series development is shown in fig. 3.

It will be noted that in this case we have a function which increases in a definite sequence of jumps at intervals of 2π. Furthermore, the asymptote of this curve is, from

Fig. 3.

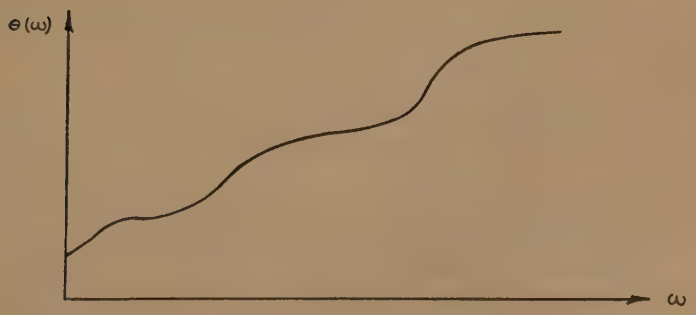


the well-known property of Fourier series development, equal to the mean square value of the function as defined by

$$\lim_{K \to \infty} \frac{1}{K} \int_0^K [f(t)]^2 \, dt.$$

More generally, however, the asymptote of the $\theta(\omega)$ graph may be shown in all cases to be equal to this mean square value without regard to the nature of the $\theta(\omega)$ "spectrum"*.

Fig. 4.



Functions which do not admit of expansion into an infinite series of trigonometric terms may, however, still admit of a similar representation by means of a $\theta(\omega)$. The $\theta(\omega)$ will, however, in this case rise gradually (except, perhaps, when line components are present), as shown in fig. 4. This

* Norbert Wiener, "On the Representation of Functions by Trigonometrical Integrals," *Math. Zeitschrift*, Bd. xxiv. Heft 3, pp. 578 and 581.

sort of a $\theta(\omega)$ is produced by random phenomena without periodicities.

3. *Analysis of Motions defined by Probability Considerations.*

In the preceding sections we have described a method of analysing irregular motions defined over a finite interval by means of a graph or other set of data. We will now give a simple example to show how the same formulæ may be employed to characterize irregular motion, analytically defined by probability conditions over an infinite time. We will give a few analytical examples utilizing *a priori* probabilities. The examples chosen involve hypotheses which suggest themselves for a preliminary study of such phenomena as telegraph spectra and static.

In all such cases we have somewhat different considerations in the computation of $\phi(u)$ than in the cases previously considered where the curve $f(t)$ was definitely defined for a given value of (t). In this case we compute the value of $\phi(u)$ by considering the *probability*, for a given typical value of t, that the value of $f(t)$ is in a certain range between A and $A+dA$ and the value of $f(t+u)$ is at the same time between B and $B+dB$. This gives us the compound probability that $\phi(u)=AB$, and by integration we shall have for the actual value of $\phi(u)$

$$\phi(u)=\int_{A=0}^{A=\infty}\int_{B=0}^{B=\infty} AB\,P(A)\,P(B)\,dA\,dB, \quad . \quad (12)$$

where A = value of $f(t)$,

B = value of $f(t+u)$,

P(A) dA = probability of value of A between A and $A+dA$,

P(B) dB = probability of value of B between B and $B+dB$.

4. *Analysis of a certain simple Sequence of Pulses closely related to Telegraph Signals.*

We are now in a position to illustrate the application of the methods outlined above to a study of such phenomena as telegraph signals. Speaking strictly, of course, a telegraph message is not a random disturbance at all, but is exactly determined by the code, the speed, and the message. From this point of view, the energy pulses corresponding to

a message of finite length could be expanded into a Fourier series with a fundamental interval equal to the length of the message. Such an analysis would, however, be laborious and would only give us a typical result as the length of the message approached infinity. We would not expect, however, long messages to differ greatly in frequency-energy distribution. In the limit this distribution would be determined by the code, the speed, and the relative probability of various letter and word combinations in the language employed. Evidently a detailed study from this point of view would be laborious indeed. In actual practice, moreover, when hand sending is employed, dots, dashes, and spaces are far from exactly equal. Investigators of this subject have gone to the other extreme of simplification in analysing a telegraph signal by considering a sequence of equally spaced dots *. Such an analysis introduces spurious lines characteristic of the assumed dot frequency, but not at all fundamental to the actual phenomena. Thus telegraph

Fig. 5.

codes employ dots, dashes, and spaces ; moreover, distinction is in some cases made between the length of dashes and spaces. In automatic systems reversals of polarity are also employed. Under these conditions an assumption of a random fall of dots and dashes not necessarily of equal length would seem to approximate more closely to actual conditions.

We will first seek the periodogram analysis of such a function which shifts from $+1$ to -1 alternately at each of an infinite series of events occurring at random with an average frequency of occurrence of a events per unit time (see fig. 5).

To begin with we will require the probability that exactly n events have occurred during the interval of time t from the instant at which the arbitrary origin of time is taken ; let the probability that exactly n events have happened be $g_n(t)$ and the average frequency of occurrence be a.

* Peters, L. J., "Behaviour of Radio Receiving Systems to Signals and to Interferences," Journ. A.I.E.E., Aug. 1926, pp. 707–716.

Then

$$\left\{\begin{array}{l}\text{Probability that zero}\\ \text{events have occurred}\\ \text{during time } t+dt\end{array}\right\} = \left\{\begin{array}{l}\text{Probability that zero}\\ \text{events have occurred}\\ \text{during the time } t\end{array}\right\} \times \left\{\begin{array}{l}\text{Probability that no}\\ \text{events occurred in}\\ \text{interval from } t \text{ to}\\ t+dt\end{array}\right\}$$

i. e., $$g_0(t+dt)=g_0(t)\times(1-a\,dt),\ \text{i. e.,}\ \frac{dg_0}{dt}=-ag_0, \quad . \quad (13)$$

or $$g_0(t)=\epsilon^{-at}. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (14)$$

Likewise, for $n\neq 0$,

$$\left\{\begin{array}{l}\text{Probability that } n\\ \text{events have occurred}\\ \text{during the time}\\ t+dt\end{array}\right\} = \left\{\begin{array}{l}\text{Probability that}\\ n-1 \text{ events have}\\ \text{occurred during the}\\ \text{time } t\end{array}\right\} \times \left\{\begin{array}{l}\text{Probability that one}\\ \text{event occurs during}\\ \text{the time } dt\end{array}\right\}$$

$$+ \left\{\begin{array}{l}\text{Probability that } n\\ \text{events have occurred}\\ \text{during the time } t\end{array}\right\} \times \left\{\begin{array}{l}\text{Probability that no}\\ \text{events occur during}\\ \text{the time } dt\end{array}\right\}$$

i. e., $$g_n(t+dt)=g_{n-1}(t)\{a\,dt\}+g_n(t)\{1-a\,dt\}, \quad . \quad (15)$$

or $$\frac{dg_n(t)}{dt}+ag_n(t)=ag_{n-1}(t), \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (16)$$

and $$g_n(t)=\frac{a^n t^n \epsilon^{-at}}{n!} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (17)$$

This result may be readily checked by substitution in the equation.

We thus have obtained in a simple manner a formula for the probability that exactly n events have occurred in a time t if the average frequency of occurrence is a.

Students of probability theory will recognize this equation as the Poisson Exponential Binomial limit widely employed by Bell System Engineers in probability computations *.

We will now utilize this result to obtain the corresponding correlation coefficient $\phi(u)$ for our random pulses.

We note that if an even number of pulses have taken place the correlation is $+1$; if an odd number take place it is -1.

We shall have, then, $\phi(u)$ equal to the sums of the probabilities that exactly zero 2, 4, 6, etc., pulses have taken place minus the probabilities that exactly 1, 3, 5, 7, etc., pulses have taken place, this gives for $\phi(u)$ †

* See in particular, Fry, T. C., 'Probability and its Engineering Uses' (Van Nostrand, 1928).

† Equation (12) for $\phi(u)$ in this case reduces merely to a summation, as A and B may assume only integral values.

$$\phi(u)=\epsilon^{-au}+\frac{a^2u^2}{2\,!}\epsilon^{-au}+\frac{a^4u^4}{4\,!}\epsilon^{-au}+\ldots$$

$$-\frac{au}{1\,!}\epsilon^{-au}-\frac{a^3u^3}{3\,!}\epsilon^{-au}-\ldots$$

or $$\phi(u)=\epsilon^{-au}\left(1-\frac{au}{1\,!}+\frac{a^2u^2}{2\,!}-\frac{a^3u^3}{3\,!}+\ldots\right). \quad . \quad . \quad (18)$$

i. e., $$\phi(u)=\epsilon^{-2au}. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (19)$$

Noting that

$$\frac{2}{\pi}\int_0^{\infty}\phi(u)\frac{\sin\omega u}{u}du=\frac{2}{\pi}\int_{u=0}^{u=\infty}du\int_{\omega=0}^{\omega=\omega}d\omega\,\phi(u)\cos\omega u,$$

we may write

$$\theta(\omega)=\frac{2}{\pi}\int_0^{\omega}d\omega\int_0^{\infty}\epsilon^{-2au}\cos\omega u\,du$$

$$=\frac{2}{\pi}\int_0^{\omega}d\omega\left[\frac{2a\,d\omega}{4a^2+\omega^2}\right]=\frac{2}{\pi}\tan^{-1}\frac{\omega}{2a}. \quad . \quad (20)$$

A plot of $\theta(\omega)$ and its derivative with respect to ω, $R(\omega)$ is shown in fig. 6. From the $\theta(\omega)$ curve (and equation 20) it will be noted that if the average duration of a pulse is $\frac{1}{a}$; half the energy is included by frequency components of frequency less than $\frac{a}{\pi}$, 90 per cent. of the energy within a frequency $7\frac{a}{\pi}$ etc. It will be noted, however, that residual energy decreases but slowly with further increase in frequency.

By noting that

$$\frac{\pi}{2}-\tan^{-1}m=\tan^{-1}\frac{1}{m},$$

and that $\tan\beta=\beta$ for small values of β, we may write

$$\operatorname*{Lim}_{\omega\to\infty}\frac{2}{\pi}\left(\frac{\pi}{2}-\tan^{-1}\frac{\omega}{2a}\right)\to\frac{4a}{\pi\omega}. \quad . \quad . \quad . \quad (21)$$

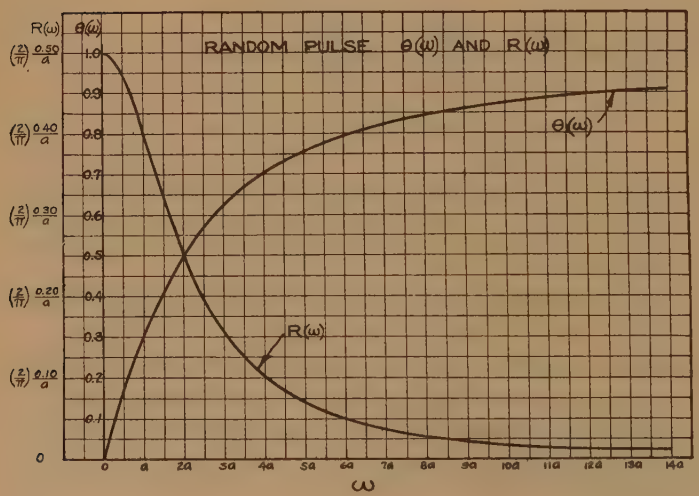
This is a very good approximation indeed when $\frac{4a}{\pi\omega}<0{\cdot}01$ so that in this case

$$[1-\theta(\omega)]\to\frac{4a}{\pi\omega}. \quad . \quad . \quad . \quad . \quad . \quad . \quad (22)$$

In other words, about 0·01 of the energy due to such a random set of pulses has a frequency greater than 130 times the average number of pulse reversals per second.

The shape of the $R(\omega)$ plot (the derivative of $\theta(\omega)$ with respect to ω) is not unlike that of a probability curve. It is of interest to note that the low frequency components receive the most energy for a given $\Delta\omega$, *i. e.*, given numerical width of frequency band. The situation is not the same, however, if the percentage width $\frac{\Delta\omega}{\omega}$ is considered. The energy in

Fig. 6.



such a band (not plotted) is proportional to $\frac{\omega}{4a^2+\omega^2}$ This function is a maximum when $\omega=2a$.

5. *The Frequency Spectrum of Static.*

Let us now consider the energy-frequency spectrum of static. Investigators of static disturbances * have disclosed that such disturbances have many of the properties of randomness which we have postulated in the previous section. Several points of departure must be considered, however, although they will prove not to be essential.

* Appleton and Watt, *loc. cit.*

It has been pointed out by Eckersley * that radio frequency energy introduced by smooth pulses of the observed durations is insufficient to account for the magnitude of static disturbances. This analysis will afford us an opportunity to re-examine this subject from a somewhat more general point of view closely related to the work of Carson; the conclusions are in essential accord with Eckersley's, but (owing to the abruptness of the pulses considered) they indicate a radio-frequency energy at the higher wave-lengths well on the border line of modern working energies. The assumptions of randomness employed should, however, apply equally well to the ripples of the static pulses. We will now consider how static pulses and the ripples thereon depart from the assumptions made in the previous section. It will be noted that :—

(*a*) Whereas we have assumed our pulses all of the same unit amplitude, the amplitude of static pulses varies widely and could better be assumed to follow a normal Gaussian probability distribution.

(*b*) We have assumed our pulses to follow continuously one after the other.

(*c*) We have assumed our pulses to be alternately of opposite sign. Neither assumption *b* nor *c* holds without modification for static.

(*d*) The assumption of a square wave-form was suggested by Appleton and Watt originally. It would also be of interest, however, to consider an exponential form.

Assumption (*a*) is quite unessential, for we may now generalize the above problem by letting the probable amplitudes of the individual pulses vary according to a normal probability function, *i.e.*,

$$P(x) = \frac{2}{\sqrt{\pi}} \epsilon^{-x^2}$$

(letting $\kappa^2 = 1$ for simplicity, *i.e.*, measuring the departure x in mean deviations). We will consider the series of causes producing the amplitude variation as independent of those

* Eckersley, T. L., "The Energy of Atmospherics," 'London Electrician,' p. 150 (Aug. 8, 1924). The greater amount of radio-frequency energy predicted from our analysis is due no doubt to the abrupt rise assumed for our square and exponential pulses. The form assumed by Mr. Eckersley rises gradually.

producing durations. Then equation (18) for $\phi(u)$ generalizes term for term to :—

$$\phi(u)=\left(\frac{2}{\sqrt{\pi}}\right)^2\left[\left(\int_0^\infty \epsilon^{-x_1^2}dx_1\right)^2\epsilon^{-au}+\int_0^\infty\int_0^\infty \epsilon^{-x_1^2}\epsilon^{-x_2^2}\frac{a^2u^2}{2\,!}\epsilon^{-au}\,dx_1dx_2-\int_0^\infty\int_0^\infty \epsilon^{-x_1^2}\epsilon^{-x_2^2}\frac{au}{1\,!}\epsilon^{-au}\,dx_1dx_2\ldots\right]. \quad . \quad (23)$$

In other words the harmonic analysis of a series of pulses such as those considered is independent of the law of chance variation of their magnitudes.

In the analysis just completed, we let chance enter into the determination of the magnitudes of our pulses, but let them be alternately positive and negative. If we let chance enter into the choice of algebraic sign, either sign being equally likely for each pulse, this will dismiss (*c*). We shall have

$$\phi(u)=\frac{4}{\pi}\left\{\left[\int_0^\infty \epsilon^{-x_1^2}dx_1\right]^2\epsilon^{-au}+\tfrac{1}{2}\sum_{n=1}^{n=\infty}\frac{(au)^{2n}\epsilon^{-au}}{(2n)\,!}\int_0^\infty dx_1\int_0^\infty dx_2\epsilon^{-x_1^2}\epsilon^{-x_2^2}-(\tfrac{1}{2})\sum_{n=1}^{n=\infty}\frac{(au)^{2n}\epsilon^{-au}}{(2n)\,!}\int_0^\infty dx_1\int_0^\infty dx_2\epsilon^{-x_1^2}\epsilon^{-x_2^2}+(\tfrac{1}{2})\sum_0^\infty\frac{(au)^{2n+1}\epsilon^{-au}}{(2n+1)\,!}\int_0^\infty dx_1\int_0^\infty dx_2\epsilon^{-x_1^2}\epsilon^{-x_2^2}-(\tfrac{1}{2})\sum_0^\infty\frac{(au)^{2n+1}\epsilon^{-au}}{(2n+1)\,!}\int_0^\infty dx_1\int_0^\infty dx_2\epsilon^{-x_1^2}\epsilon^{-x_2^2}\right\}, \quad . \quad . \quad . \quad (24)$$

or $\phi(u)=\epsilon^{-au}$,

i. e., the effect of allowing a random choice of sign is to halve the frequency scale of the previous analysis, which seems reasonable from *a priori* consideration.

We may now proceed to a consideration of a general series of pulses falling individually and collectively at random, and with an average frequency of a per second. We have demonstrated that the conclusions thus derived are independent of the normal law chosen to represent the probable distribution of the amplitudes. We shall need the following simple and very interesting lemma.

Lemma.

In a series of random *independent* pulses, *equally likely to be positive or negative**, the correlation between different pulses is zero. (This property is independent of whether the pulses do or do not overlap.)

Let $f(A_1, t)dA_1$ be the probability that a certain pulse has a value of A_1 (between A_1 and A_1+dA_1, of course) at a given instant t. Now, since any pulse is equally likely to be positive or negative, $f_1(A_1t)=f_1(-A_1, t)$ for all values of t, $f_1(A_1, t)$ is an even function of A_1. Hence, $A_1f(A_1, t_1)$ is an odd function of A_1 for all values of t_1. Likewise for any other pulse $A_2f(A_2, t_2)$ is an odd function of A_2 for all values of t_2.

Now (from equation (12)) the correlation for the displacement interval (u),

$$\phi(u) = \operatorname*{Lim}_{B\to\infty} \frac{1}{2B}\int_{t=-B}^{t=B} dt\left\{\int_{-\infty}^{\infty} dA_1 \int_{-\infty}^{\infty} dA_2(A_1A_2)f_1(A_1, t) \times f_2(A_2, t+u)\right\}$$

$$= \operatorname*{Lim}_{B\to\infty} \frac{1}{2B}\int_{t=-B}^{t=B} dt\left\{\int_{-\infty}^{\infty} A_1 f_1(A_1, t)dA_1\right\}\left\{\int_{-\infty}^{\infty} A_2 \times f_2(A_2, t+u)dA_2\right\} \quad . \quad (25)$$

Since $A_1f_1(A_1, t_1)dA_1$ and $A_2f_2(A_2, t+u)dA_2$ are both *odd* functions, their integrals between $+\infty$ and $-\infty$ vanish, hence

$$\phi(u) = \operatorname*{Lim}_{B\to\infty} \frac{1}{2B}\int_{-B}^{B} dt\{0\}\{0\} = 0.$$

An important consideration, entering into the frequency characterization of static as a random sequence of pulses, is to be sure that no false basic periodicities are introduced by the choice of a definite constant duration of pulse or any but a random law of occurrence.

In the preceding discussion we have seen, then, how the frequency spectrum of a continuous sequence of pulses, initiated at random instants and of an amplitude following any normal probability law, may be determined. The frequency spectrum is continuous, and the value of $\theta(\omega)$ is indeed given by the surprisingly simple formula

$$\theta(\omega) = \frac{2}{\pi}\tan^{-1}\frac{\omega}{2a}, \quad . \quad . \quad . \quad . \quad . \quad (26)$$

* This theorem is not true unless this condition is fulfilled.

where a=the average frequency of occurrence of the random pulses.

This formula, with the generalization permitted by the above discussion, is nearly, if not quite, adequate to characterize the frequency distribution of static. In the closing pages of this paper, however, we will consider the analysis for the spectrum of a series of pulses of an exponential wave form falling at random with an average frequency of occurrence of n per second. We will show that the conclusions obtained from a consideration of the square pulse wave-forms are not essentially altered. We may also show by a similar attack that the conclusions are essentially the same for a series of square pulses spaced far apart and of variable duration.

6. *Analysis of Exponential Pulses.*

In carrying out this analysis we will first compute the value of the correlation function $\phi(u)$ for a random sequence of pulses having the form $f(t)=\epsilon^{-\beta t}$ for a given value of β; this we denote by $\phi_\beta(u)$. We will then compute a mean $\phi(u)$ by letting β vary according to a normal probability law round a mean value.

We have

$$\phi_\beta(u)=\frac{n\mathrm{T}}{\mathrm{T}}\int_0^\infty f(t)f(t+u)dt=\frac{n\epsilon^{-\beta u}}{2\beta}. \quad . \quad . \quad . \quad (27)$$

From (p. 187) we note that a $\phi(u)$ of this form will give us a

$$\mathrm{R}_\beta(\omega)=\frac{1}{\pi}\frac{n}{\beta^2+\omega^2}. \quad . \quad . \quad . \quad . \quad . \quad . \quad (28)$$

We will now assume a normal probability variation of the β's around a mean β_0. Then the probability of a β between β and $\beta+d\beta$;

$$\mathrm{P}(\beta)=\frac{2\kappa}{\sqrt{\pi}}\,\epsilon^{-\kappa^2(\beta-\beta_0)^2}d\beta.$$

Expanding $(\mathrm{R}_\beta(\omega)$ into a series form, and making one or two obvious changes of variable and transformations, we have

$$\mathrm{R}_\beta(\omega)=\frac{1}{\pi}\frac{n}{\omega^2}\frac{1}{1+\frac{\beta^2}{\omega^2}}$$

$$=\frac{1}{\pi}\frac{n}{\omega^2}\left[1-\frac{\beta^2}{\omega^2}+\frac{\beta^4}{\omega^4}-\ldots\right]. \quad . \quad (29)$$

Now varying the β's and noting

$$\left[\mathrm{R}(\omega)\right] = \int_{\beta=0}^{\beta=\infty} \mathrm{R}_\beta(\omega)\, \mathrm{P}(\beta)\, d\beta,$$

$$\left[\mathrm{R}(\omega)\right]_{\text{mean}} = \frac{1}{\pi}\frac{n}{\omega^2}\left[\int_0^\infty \frac{2\kappa}{\sqrt{\pi}} \epsilon^{-\kappa^2(\beta-\beta_0)^2}\, d\beta - \int_0 \frac{2\kappa}{\sqrt{\pi}} \frac{\beta^2}{\omega^2}\, \epsilon^{-\kappa^2(\beta-\beta_0)^2}\, d\beta + \dots\right]$$

$$\mathrm{R}(\omega) = \frac{1}{\pi}\frac{n}{\omega^2}\left[1 - \frac{\beta_0^2}{\omega^2}\left(1 + \frac{1}{\sqrt{\pi}}\frac{2}{\beta_0\kappa} + \frac{1}{2\kappa^2\beta_0^2}\right) + \dots \text{. higher powers of } \left(\frac{\beta_0}{\omega}\right)\right].$$

Now in the case of our radio static we have for order of magnitudes:—

$$n = 1 \text{ to } 100,$$

$$\beta_0 = 10^3 \text{ sec.}^{-1},$$

$$\omega = \frac{2\pi}{\mathrm{T}} = \frac{2\pi(3\times10^8)}{\lambda} \text{(metres, seconds)}.$$

$$\therefore\ \mathrm{R}(\omega) = \frac{1}{\pi}\frac{n\lambda^2}{\left[(2\pi)(3\times10^8)\right]^2} \times\left[1 + \dots + \text{terms of higher order in } \frac{\lambda}{(2\pi)(3\times10^8)}\right].$$

It thus appears that, for static frequencies of the order of magnitude assumed, the energy distribution of static varies nearly as the square of the wave-length *.

The same conclusion follows with but slight modification in analysis for the previous assumption of square waves with a random frequency of occurrence, provided we let the average frequency of reversal approach the reciprocal of the average lengths of duration observed. The foregoing considerations lead us strongly to suspect that this property probably holds a considerable range of frequencies for most forms of impulsive physical discharges.

* Provided ($\lambda < 100{,}000$ metres) and for a given width of frequency band $\Delta\omega$ (not a given $\Delta\lambda$). In terms of λ alone, since

$$|\, d\omega\,| = \left|\frac{(2\pi)(3\times10^8)d\lambda}{\lambda^2}\right|,$$

$$\mathrm{R}_{d\lambda}(\lambda) = \frac{1}{\pi}\frac{n^1}{(2\pi)(3\times10^8)}.$$

7. *Summary and Conclusions.*

From the above analysis we see that the energy contained within a frequency band of given width due to a static produced by a random sequence of pulses of the forms investigated would vary directly with the square of the wave-length.

This result is in accord with Austin's early conclusions in the investigation of static on long waves *, where he found the fields (proportional to the square roots of the energies) to vary roughly as the first power of the wave-length. The possibility of explaining the observed results from this point of view was qualitatively suggested by Pickard in a discussion of the paper †.

From equation (31) we may investigate quantitatively the fraction of the energy due to the sequence of pulses in a given frequency band $\Delta\omega$. For simplicity we will confine ourselves to the exponential pulse case. The conclusions in all cases are essentially the same.

Note in this case

$$\text{Total Power} = \theta(\infty) = \lim_{T\to\infty} \frac{1}{T}\int_0^T [f(t)]^2 dt$$

$$= \frac{nT}{T}\int_0^\infty dt\,\epsilon^{-2\beta t}\int_{\beta=0}^{\beta=\infty} P(\beta)d\beta = n\int_{\beta=0}^{\beta=\infty}\frac{P(\beta)}{2\beta}d\beta$$

$$= \frac{n}{2}\left(\frac{1}{\beta}\right)_{\text{mean}} = \frac{n}{2}\frac{1}{\bar{\beta}} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (32)$$

$$\therefore \quad \frac{(R\omega)}{\theta(\infty)} = \frac{1}{\pi}\frac{2\bar{\beta}\lambda^2}{[2\pi(3\times 10^8)]^2} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (33)$$

Using the magnitude $\bar{\beta} = 10^3$ sec.$^{-1}$, this gives us something of the order of 10^{-4} as the total received *energy* of a static pulse of duration of the order of 10^{-3} second in a frequency width of 5000 cycles on 10,000 metres; at 1000 metres this fraction (varying with the square of the wave-length) has diminished to 10^{-6} and at 100 metres to 10^{-8}. It will be noted that, when the average duration of the pulse is long compared with the natural period of the signals in the given frequency band, halving the average duration of the pulses doubles the energy in the band, *provided* the root mean square value of the static remains constant, for this means the *number* of pulses must increase in direct proportion.

From the above analysis it appears that the energy due to gross outline of pulses of the order of 10^{-3} second in

* Austin, L. W., "The Relation between Atmospheric Disturbances and Wave-Length in Radio Reception," Proc. I. R. E. ix. pp. 28-70 (February 1921).

† Pickard, G. W., Discussion on Austin's paper (*loc. cit.*), Proc. I. R. E. p. 36 (1921).

duration and square or sharply rising exponential form, can produce appreciable fields (proportional to the square roots of the energies) on the longer wave-lengths employed in practice, but that on the shorter waves pulses or ripples of smaller energy content but shorter duration will be increasingly important. Thus, as indicated by the square-wave investigation, a series of pulses of $\frac{1}{n}$ the energy content but n times the rate of reversal will produce the same high frequency energy. (See equation 22.)

It will be noted that the methods employed in this paper are not confined in their application to the examples given (which are merely illustrations of the methods), but are useful in the harmonic analysis of many other types of irregular motions, such as voice waves, or noise.

Appendix A.

The final formula for $\theta(\omega)$ which we employ in our computations is as follows :—

$$\theta(\omega) = \frac{2}{\pi}\int_0^\infty \frac{\sin \omega u}{u}\,du\left[\lim_{K\to\infty}\frac{1}{K-u}\int_0^{K-u} f(y)f(y+u)\,dy\right] \quad . \quad . \quad . \quad (1\,b)$$

(repeated)

In this formula it will be recalled that $f(y)$ is the function under analysis and K is the length of the interval. This formula for $\theta(\omega)$, which we employ, appears in somewhat generalized and modified form in Wiener's paper *. (See p. 121; Equation (47).)

Wiener obtains a function $R(f; u)$, which is, for the special case of well-behaved functions †, exactly equal to twice our function $\theta(\omega)$.

$R(f; u)$ is given in his notation by the equation ‡

$$R(f; u) = \frac{2}{\pi}\int_0^\infty \left\{\frac{3}{\pi}\lim_{h\to\infty} \int_{-\infty}^{\infty} \frac{\sin^4 ht}{t^4} f\left(t+\frac{\alpha}{2}\right)f\left(t-\frac{\alpha}{2}\right)dt\right\}\frac{\sin \alpha u}{u}\,d\alpha. \quad . \quad . \quad . \quad (A\,1)$$

* Norbert Wiener, "The Quadratic Variation of a Function and its Fourier Coefficients," M. I. T. Bulletin, Dept. Math. Ser. 2, No. 75, March 1924.

† Norbert Wiener, "On the Representation of Functions by Trigonometrical Integrals," *Math. Zeitschrift*, Bd. 24, Heft 3, pp. 575–616; also M. I. T. Bulletin, Dept. Math. Ser. 2, No. 108.

‡ Norbert Wiener, "The Harmonic Analysis of Irregular Motion," Journal of Math. and Physics, v. Nos. 2 and 3, February and March 1926.

In order to throw equation (A 1) into the form we shall use, however, we need several substitutions and changes of variable.

Wiener establishes, on p. 119 (Equation (44)), that

$$\int_0^\infty \cos 2\omega u \, d\{\mathrm{R}(f;u)\} = \frac{3}{\pi} \lim_{h\to 0} \frac{1}{h^3} \int_{-\infty}^{\infty} \frac{\sin^4 ht}{t^4} f(t+\omega) f(t-\omega)\, dt. \quad . \quad . \quad . \quad (\mathrm{A}\,2)$$

Now if

$$\lim_{\mathrm{A}\to\infty} \frac{1}{2\mathrm{A}} \int_{-\mathrm{A}}^{\mathrm{A}} f(t+\omega) f(t-\omega)\, dt$$

exists, we have (p. 119 (1))

$$\tfrac{1}{2} \int_0^\infty \cos 2\omega u \, d\mathrm{R}(f;u) = \lim_{\mathrm{A}\to\infty} \frac{1}{2\mathrm{A}} \int_{-\mathrm{A}}^{\mathrm{A}} f(t+\omega) f(t-\omega)\, dt. \quad . \quad . \quad . \quad (\mathrm{A}\,3)$$

Multiplying equation (A 3) by two and equating the right-hand member thus obtained to the right-hand member of equation (A 1) (Wiener's equation (44), p. 119 (12)), we have

$$\frac{3}{\pi} \lim_{h\to 0} \frac{1}{h^3} \int_{-\infty}^{\infty} \frac{\sin^4 ht}{t^4} f(t+\omega) f(t-\omega)\, dt = 2 \lim_{\mathrm{A}\to\infty} \frac{1}{2\mathrm{A}} \int_{-\mathrm{A}}^{\mathrm{A}} f(t+\omega) f(t-\omega)\, dt. \quad . \quad . \quad (\mathrm{A}\,4)$$

Substituting equation (A 4) in equation (A 1) gives :—

$$\mathrm{R}(f;u) = \frac{2}{\pi} \int \frac{\sin \alpha u}{\alpha} d\alpha \left\{ 2 \lim \frac{1}{2\mathrm{A}} \int_{-\mathrm{A}}^{\mathrm{A}} f\left(t+\frac{\alpha}{2}\right) f\left(t-\frac{\alpha}{2}\right) dt \right\}. \quad . \quad . \quad . \quad (\mathrm{A}\,5)$$

Letting $t - \frac{\alpha}{2} = v$, and then altering variables of integration by letting $\alpha = u$ and $u = \omega$ in equation (A 5), gives, in the notation we have adopted,

$$\mathrm{R}(f;u) = \frac{2}{\pi} \int_0^\infty \frac{\sin \omega u}{u} du \left\{ 2 \lim_{\mathrm{A}\to\infty} \frac{1}{2\mathrm{A}} \int_{-\mathrm{A}-\frac{u}{2}}^{\mathrm{A}-\frac{u}{2}} f(v+u) f(v)\, dv \right\}. \quad . \quad (\mathrm{A}\,6)$$

If, now, y is the distance from the left-hand end of our graph (*i. e.*, the smallest value of v for which our function is defined) and K the length of our interval, we have, in our notation,

$$\theta(\omega) = \frac{2}{\pi} \int_0^\infty \frac{\sin \omega u}{u} du \left\{ \lim_{\mathrm{K}\to\infty} \frac{1}{\mathrm{K}-u} \int_0^{\mathrm{K}-u} f(y) f(y+u)\, dy. \right. \quad . \quad . \quad . \quad (\mathrm{A}\,7)$$

XX. *Beryllium Spectrum in the Region* λ 3367–1964. *By* S. N. Bose, *Professor of Physics, Dacca University, and* S. K. Mukherjee, *Assistant Lecturer in Physics, Dacca University* *.

[Plates II. & III.]

THE beryllium spectrum is remarkable owing to the small number of lines that have been observed in the visible and the ultra-violet. The earlier measurements are somewhat conflicting. Exner and Haschek could not find some of the lines observed by Rowland and Tatnall †. Glaser ‡ investigated the spectrum by sparking between the metal tips, but he also could not corroborate the earlier observations.

Recently Millikan and Bowen § subjected the spectrum to a thorough analysis by their method of hot spark, and extended it up to 1943 Å.U. They classified some of the important lines, and gave the term values both of Be II and Be I.

It was with a view to study the spectrum thoroughly, under different conditions of excitation, that the present work was undertaken.

The instrument that we have used almost exclusively for the work is Hilger's Quartz Spectrograph, type E 1. In the near ultra-violet between the regions 2400–1850 it is almost an ideal instrument for spectrum analysis, combining a high dispersion with a high light-value. We have extended our observations to the visible region ; but here, because of the low dispersion, the measurements were not more accurate than by ·1 Å.U., though we could very easily identify the lines and thus verify the observations of the previous workers.

Most of the observations were made on the arc spectrum, and obtained by feeding the nitrate or the metal in a carbon arc. We have used both ordinary and Hilger's extra pure carbon rods, and the presence of traces of iron has been an advantage in furnishing suitable standard lines in the different regions. In the extreme ultra-violet we have used copper arc and spark as comparison spectra, and in some cases the silicon lines almost always present in carbon spectra were helpful in making accurate measurements.

The plates used were Ilford Empress and Ordinary up to 2175. In the extreme ultra-violet we tried sensitization with

* Communicated by the Authors.

† Kayser, *Handbuch d. Spectro.* vol. v.

‡ Glaser, *Ann. d. Phys.* (4) lxviii. pp. 73–88 (1922).

§ Millikan and Bowen, Phys. Rev., Aug. 1926.

machine oil, but the lines were a little broad. As our aim was to resolve very narrow doublets, we could only get the best results by using Schumann plates as supplied by Hilger.

The materials used were, at first, certain old samples of beryllium nitrate and metal from Merck's, which were found to contain lead, aluminium, and silver as impurities. Later, owing to the kindness of Professor Mark, of Badische Anilin Fabrik, we were enabled to get a different sample of the metal. But this was found to contain traces of rare earths, notably scandium and yttrium. By a comparison of the different samples the lines due to contamination were eliminated, and we give our results tabulated below (*vide* Table I.).

As may be seen, we could go almost to the same limit as Millikan and Bowen by their hot-spark method, and, incidentally, we have discovered that the following lines, 2351, 2175, 2126, 2056, and 2033, given as singlets by Millikan and Bowen, are clearly doublets of approximate wave-number difference 2·6. Most probably these are triplets due to the triplet P-terms, and our spectrograph could only separate P_1 from P_2+P_3. The wave-number difference thus measured is the distance of P_1 from the centre of gravity of P_2- and P_3-lines, and as such has a slightly higher value. The lines 1998 and 1964 just appeared as doublets, but owing to their hazy character the measurements of the doublet separation were not possible. We could verify the earlier measurements of Rowland and Tatnall as well as the line of Glaser, viz. λ 4672·9. Incidentally, we have discovered a few new lines whose wave-lengths are given in Table I. The line 3019 appeared as a doublet, the line 2986 as a triplet, and the lines 3110 and 2738 as singlets.

We have made some observations by feeding a fair amount of metal or the salt in the arc, and we could observe that the lines 3321, 2651, 2494, and 2175 with their components were reversed in some cases, thus showing that the p-level is probably the common origin of the lines as classified by Millikan and Bowen. In rare occasions, however, the line 3131, usually attributed to Be II, could be reversed. The line 2348 (1 S–2 P) is always reversed in the arc.

We have tried the spark spectra in air, where, owing to rapid oxidation, we could make very little progress. We have also tried sparking between the tips of the metal, enclosed in a partially evacuated vessel with quartz window; and even then we could not go beyond 2175. In this way, however, we have got an interesting band spectrum, which we believe to be due to beryllium and which consists of bands degraded to the red. The fine structures of the band have

not yet been measured, and we give in Table II. the measurements of the edges.

There does not seem to be any line of Be between 4700 up to the extreme red. We are now continuing the work in the infra-red, and hope to be able to corroborate the solitary work of Theo Volk * in the region.

The following table gives the wave-lengths (in I. *a*, vac.) of the lines between λ 3367–1964, with the frequency difference between the components, and also the lines (in I. *a*) of Rowland and Tatnall, together with the few lines marked * observed by us as new :—

TABLE I.

Bose & Mukherjee.	Rowland & Tatnall. I. *a*.	Bowen & Millikan. I. *a*, vac.	$\delta\nu$.
3367·55	3367·579	—	—
*3110·91	—	—	—
*3019·54	—	—	—
*3019·33	—	—	—
2986·63	—	—	—
2986·44	2986·426	—	—
2986·08	2986·057	—	—
2898·26	2898·242	—	—
*2738·08	—	—	—
2351·40 2351·54	—	2351·50	2·50
2175·72 2175·84	—	2175·72	2·64
2126·30 2126·42	—	2126·57	2·66
2056·65 2056·77	—	2056·71	2·60
2033·23 2033·34	—	2033·43	2·66
1998 (*a*)	—	1998·19	
(*a*)	—	1964·81	

The lines marked (*a*) appear in plates, but their measurements are unsatisfactory owing to the absence of standards in this region.

In the accompanying plates (Pls. II. and III.) I. and III. are contact-prints from Schumann plates; II. and IV. (*a*) are microphotographic enlargements for showing the fine structure ; IV., contact-print from ordinary plate ; V. and VI. are slightly enlarged prints to show the new lines.

The following table gives the wave-lengths (in I. *a*) of the

* Dissert. Tübingen, 1924 (Dresden bei Teubner). 17 pp.

edges of the band; those marked (*a*) are fully developed with their fine structures :—

Table II.

1.....	2474·2	6.....	2285·8
2 (*a*)	2446 0	7.....	2260·8
3 (*a*)	2419·2	8.....	2238·3
4 (*a*)	2325·1	9.....	2221·7
5 (*a*)	2299·4	10 (*a*)	2189·0

XXI. *Frequency Variations of the Triode Oscillator. A Reply to* Mr. D. F. Martyn, *B.Sc., A.R.C.Sc. By* Lt.-Col. K. E. Edgeworth, *D.S.O., M.C., A.M.I.E.E.**

IN the April number of the Philosophical Magazine there appeared a note of mine under the above title, in which I comment on a paper by Mr. D. F. Martyn (Phil. Mag., Nov. 1927), also with the same title. In my note I direct attention to a paper which I read before the Institution of Electrical Engineers (Wireless Section) on the 6th of January, 1926, and I remark: "So far as they cover the same ground, the experimental results appear to be in agreement, and the explanations offered are substantially the same. The main cause of frequency variations is associated with damping of one sort or another in the grid circuit, and, other things being equal, the magnitude of the frequency variation is proportional to the amount of damping. This type of frequency variation is referred to in my paper as a frequency variation of the first type."

In a further paper on the same subject (Phil. Mag., July 1928) Martyn rejects my statement, and it is necessary therefore that I should prove my words.

If a reference is made to my paper it will be found that seven different classes of circuit are dealt with :—

(i.) Tuned grid and tuned anode with normal coupling.
(ii.) Tuned grid and tuned anode with reversed coupling.
(iii.) Tuned grid and tuned anode with resistance coupling.
(iv.) Tuned grid and untuned anode with normal coupling.
(v.) Untuned grid and tuned anode with normal coupling.
(vi.) Tuned grid and untuned anode with reversed coupling.
(vii.) Untuned grid and tuned anode with reversed coupling.

No general solution is offered to cover all these different classes of circuit, but each class is dealt with separately.

* Communicated by the Author.

Formulæ for frequency variations of the first type applicable to circuits of classes (i.) and (ii.) are given in equations (7), (8), (18), and (19) of my paper, attention being paid in each case to the appropriate sign.

The frequency variation of the first type is absent from resistance coupled circuits—Class (iii.).

A formula for the frequency variation of the first type applicable to circuits of class (iv.) is given in equation (20).

A formula for the frequency variation of the first type applicable to circuits of class (v.) is given near the end of my reply to the discussion.

Formulæ for the remaining two classes of circuit are not given, but can easily be obtained by the methods indicated in the paper.

Martyn tries to apply equation (8) to explain his experimental results, whereas this equation is obtained on the assumption that $L_1C_1 = L_2C_2$ and is clearly applicable to circuits of classes (i.) and (ii.) only.

The circuit used by Martyn in his experiments is a circuit with an untuned grid coil, and it belongs therefore to class (v). The equation given in my reply to the discussion is :

$$f = \frac{1}{2\pi\sqrt{L_1C_1}}\left\{1+\frac{1}{2A}\left(R_1-\frac{R_2C_2}{C_1}\right)-\frac{R_1R_2C_2}{2L_1}\right\}. \quad (A)$$

Where $R_2C_2 = R_1C_2 + L_2\sigma/G$: as explained in the note immediately following equation (18).

If R_4 (the resistance of the grid coil) is neglected the equation reduces to

$$f = \frac{1}{2\pi\sqrt{L_1C_1}}\left\{1+\frac{1}{2A}\left(R_1-\frac{L_2\sigma}{C_1G}\right)-\frac{R_1L_2\sigma}{2L_1G}\right\}. \quad (B)$$

The equation is derived on the assumption that the variation is small compared with the natural frequency $1/\sqrt{L_1C_1}$.

Martyn's equation (8) is

$$p^2 = \frac{1}{L_1C_1 + k_1k_3(L_1L_2 - M^2)}. \quad . \quad . \quad . \quad (C)$$

The equation is obtained on the assumption that the resistance of the anode coil is negligible.

The equations cover common ground when both assumptions are admissible.

Applying the second assumption to equation (B)—that is to say, putting $R_1 = 0$,—

$$f = \frac{1}{2\pi\sqrt{L_1C_1}}\left\{1-\frac{L_2\sigma}{2AC_1G}\right\}. \quad . \quad . \quad . \quad (D)$$

Applying the first assumption to equation (C)—that

is to say, assuming that $k_1k_3(L_1L_2-M^2)$ is small compared with L_1C_1,—

$$p = \frac{1}{\sqrt{L_1C_1}}\left\{1-\frac{k_1k_3(L_1L_2-M^2)}{2L_1C_1}\right\}. \quad . \quad . \quad . \quad (E)$$

Observing that $\sigma = 1-M^2/L_1L_2$; $p = 2\pi f$; $A = 1/k_1$; $G = 1/k_3$, it is clear that equation (D) is identical with equation (E).

The identity of these two equations provides a formal proof that the frequency variation investigated by Martyn is the same as the frequency variation of the first type discussed in my paper, and justifies the statement in my previous note which is quoted at the head of this paper.

Most of the points discussed in Martyn's first paper—the significance of the quantity $k_1k_3(L_1L_2-M^2)/L_1C_1$ or $L_2\sigma/(AGC_1)$, the conditions of minimum variation, and so on—can be derived from any of the above equations with equal facility.

The following quotations are also significant:—Martyn, "The most important cause of frequency variations is found to be the flow of grid current"; Edgeworth, "The damping in the grid circuit is of fundamental importance, since it determines the whole scale on which the frequency variations occur."

I should now like to offer some comments on the latter part of Martyn's second paper, in which he describes in some detail his efforts to reduce the frequency variations to a minimum. He claims that "the frequency remained constant to one part in 100,000, *even when the filament current was deliberately varied*, . . ." (Martyn's italics). I wish to state that results of precisely the same order were demonstrated to me by the engineers of the Marconi Company early in 1925. I believe that a grid leak of 2 or 3 megohms was used in conjunction with the usual grid leak condenser.

The results of my own experiments, which were carried out shortly after the above demonstration, are shown in fig. 22 of my paper. The filament voltage was varied from 3·8 to 4·2, and the resulting frequency variations were:—

With no grid leak	1 in 1,000
With a grid leak of ·02.....	1 in 2,500
With a grid leak of ·1	1 in 12,000
With a grid leak of ·5	1 in 40,000

The use of larger grid leaks is not mentioned, but it is surely evident that the use of a larger grid leak would reduce the frequency variation still further.

As a matter of fact not very much use has been made of

these results. The main difficulty about the valve oscillator as a standard of frequency is that it is very difficult to keep the capacity of the circuit constant under ordinary working conditions, more especially if the oscillator is required to drive another valve circuit.

For this reason the valve driven tuning-fork and the valve oscillator with crystal control seem to have captured most of the field. The results obtainable by these methods are constantly referred to in current wireless periodicals, and need not be described in detail here.

XXII. *The Raman Spectra of Scattered Radiation.*

To the Editors of the Philosophical Magazine.

Gentlemen,—

In the October number of the Philosophical Magazine (1928) Prof. R. W. Wood gives important new data confirming the discovery of Raman that the frequency difference between the companion line and the exciting line is constant and equal to the frequency of an infra-red absorption band. Since his calculated infra-red absorption bands of calcite lack comparative data based upon direct observations, the following tabulations may be of interest :—

Benzol— Calculated from scattered radiation.		Observed by Coblentz.	
Raman.	Wood.		
3·27 μ	3·27 μ	3·25 μ	
6·28	6·23 & 6·30	6·25	Complex.
8·57	8·55	8·67 (8·5 to 8·7)	Complex.
10·10 } 10·13 }	10·05 } 10·15 }	10·0 to 10·3	Complex.
11·78	11·78	11·8	
Calcite—	5·78	5·8	Complex.
	9·19	9·2	
	14·	14·1	(Obs. by Nyswander).

The direct observations on calcite are taken from papers by Coblentz and by Nyswander; those on benzol were obtained by Coblentz. Owing to the small dispersion, the absorption bands of calcite at 5·8 μ and 9·2 μ, also of benzol at 6·25 μ, 8·6 μ, and 10·2 μ, are not completely resolved. Taking this into consideration, the agreement between the calculated and the observed values is as good as can be expected until we can obtain new infra-red measurements.

Bureau of Standards,
Washington, D.C.
October 29, 1928.

Respectfully submitted,
W. W. Coblentz.

XXIII. *On the Intensity of the Scattered Light from an Unpolarized Beam.*

To the Editors of the Philosophical Magazine.

Gentlemen,—

Rayleigh gives in his original memoir on light-scattering from small particles (Phil. Mag. xli. p. 113, 1871) the following expression for the intensity of scattered light from a volume element containing m particles when the primary beam is unpolarized:

$$A^2\frac{(D'-D)^2}{D^2}(1+\cos^2\beta)\frac{mT^2}{\lambda^4 r^2},$$

where A^2 is the intensity in the primary beam. Rayleigh points out later that a factor π^2 was omitted and the expression should be

$$A^2\frac{(D'-D)^2}{D^2}(1+\cos^2\beta)\frac{mT^2\pi^2}{\lambda^4 r^2}.$$

By integrating over a sphere the coefficient of attenuation of the primary beam is obtained in the form

$$h=\frac{16}{3}\pi^3\frac{mT^2}{\lambda^4}\frac{(D'-D)^2}{D^2},\quad (I=I_0e^{-hx}),$$

where m is now the number of particles per unit volume of the turbid medium. This differs from the result derived by Rayleigh (Phil. Mag. xlviii. p. 377, 1899) for a polarized beam, namely

$$h=\frac{8\pi^3}{3}\frac{mT^2}{\lambda^4}\frac{(D'-D)^2}{D^2}$$

by the factor 2. The coefficient of attenuation for polarized and unpolarized beams must, however, be the same. On checking the integration leading to the expression (1), it appears that Rayleigh has inadvertently omitted a factor of $\frac{1}{2}$, and (1) should run

$$\frac{A^2}{2}\frac{(D'-D)^2}{D^2}(1+\cos^2\beta)\frac{m\mathrm{T}^2\pi^2}{\lambda^4 r^2}.$$

Rayleigh bases none of his later work on formula (1), so that the error is not propagated. Other writers have used the result, however, and it may be useful to draw attention to the amendment necessary.

The unamended result is reprinted in Rayleigh's 'Collected Works,' Wood's 'Physical Optics,' and other standard works.

Yours faithfully,
W. S. Stiles.

XXIV. *The Constant of Mass Action.*

To the Editors of the Philosophical Magazine.

Gentlemen,—

In a recent communication (Phil. Mag. ser. 7, v. p. 263, 1928) R. D. Kleeman develops an expression for the Constant of Mass Action differing in a fundamental particular from the van't Hoff equation.

In his equation (6) (*loc. cit.* p. 267),

$$\begin{aligned}\mathrm{RT}\ln\frac{(p_C'')^c(p_D'')^d}{(p_A'')^a(p_B'')^b} = \mathrm{RT}\ln\frac{(p_C')^c(p_D')^d}{(p_A')^a(p_B')^b}\\ +\Big[c\mathrm{RT}\ln \mathrm{C}' + c\Sigma\frac{-\mathrm{C}_n}{(n-1)(\mathrm{C}'p_C')^{n-1}}\\ -c\mathrm{RT}\ln \mathrm{C}'' - c\Sigma\frac{-\mathrm{C}_n}{(n-1)(\mathrm{C}''p_C'')^{n-1}}\\ +d\mathrm{RT}\ln \mathrm{D}' + d\Sigma\frac{-\mathrm{D}_n}{(n-1)(\mathrm{D}'p_D')^{n-1}}\\ -d\mathrm{RT}\ln \mathrm{D}'' - d\Sigma\frac{-\mathrm{D}_n}{(n-1)(\mathrm{D}''p_D'')^{n-1}}\Big],\end{aligned}$$

the factor in the square brackets has been obtained on the assumption that in the removal of the "sepro-unstable" molecules, C and D, from the equilibrium box, they dissociate into their equilibrium mixture, so that the pressures

between which they are compressed are not p_C'', p_C', p_D'', p_D', as van't Hoff supposed, but terms depending on the degree of dissociation.

I would point out that Kleeman has not considered the free energy decrease in the dissociation of these "sepro-unstable" molecules on removal from reservoir II., from the pressures p_C'', p_D'', to the equilibrium mixtures at the pressures $C''p_C''$, $D''p_D''$, and the free energy increase required to convert the equilibrium mixtures at pressures $C'p_C'$, $D'p_D'$, to the "sepro-unstable" molecules at pressures p_C', p_D', on return to reservior I. These free energy terms are not equivalent, and if they are considered it can be shown very simply by the usual methods of thermodynamics that the free energy increase in transferring c molecules of C from a pressure p_C'' to a pressure p_C' is $c\mathrm{RT}\ln\frac{p_C'}{p_C''}$, and that the similar term for D is $d\mathrm{RT}\ln\frac{p_D'}{p_D''}$. The Constant of Mass Action then reduces to the simple van't Hoff form. It may be emphasized here that the free energy change in any alteration of a system between given states is independent of the path chosen, provided that every process in the path is carried out under isothermal and reversible conditions.

In the conclusion of his paper Kleeman puts forward kinetic evidence in support of his new Constant of Mass Action which is substantially the kinetic theory proof of the Law of Mass Action in terms of activities (compare H. S. Taylor, 'Treatise on Physical Chemistry' (1924), vol. i. p. 299). Kleeman's factor κ is not a correction for the velocity of reaction k, but is the activity coefficient of the concentration term.

Yours faithfully,

R. F. Goldstein.

Crumpsall, Manchester.
Sept. 29th, 1928.

XXV. *The Constant of Mass Action.*

To the Editors of the Philosophical Magazine.

Gentlemen,—

MR. GOLDSTEIN, in his criticism of my paper on the Constant of Mass Action in the preceding letter to this Journal, states that the changes in free energy on

removing dissociating molecules from the reservoirs of a van't Hoff cycle do not vanish, and that if these changes are taken into account van't Hoff's result is obtained. He does not, however, show how this is done. May I point out that in the van't Hoff cycle it is usually supposed that the conditions are such that no change in the partial pressure of the kind of molecules in a reservoir takes place of which a small fraction is removed, which will then also hold for the pressure in the cylinder used for removing them independently of dissociation, in which case the change in free energy is zero, since $\partial p = 0$. The removed molecules will tend to be replaced by a resultant association or dissociation taking place in the mixture, depending on whether or no these molecules dissociate after removal. I may add that we may assist, if we like, in maintaining the partial pressures constant by means of various agents and conditions ; thus, for example, we may suppose that a part of the reservoir contains a substance which occludes in part the gaseous mixture etc.

This letter gives me an opportunity to point out that the result I have obtained may be deduced more simply by equating to zero the external work done during the cycle (or equating the work along two different paths) instead of the change in free energy. Referring to my paper (Phil. Mag. v. p. 263, 1928), this gives

$$a\mathrm{RT} + b\mathrm{RT} + a\int_{p_{A'}}^{p_{A''}} p \cdot \frac{\partial v}{\partial p} \cdot \partial p + b\int_{p_{B'}}^{p_{B''}} p \cdot \frac{\partial v}{\partial p} \cdot \partial p - a\mathrm{RT} - b\mathrm{RT}$$

$$= c\mathrm{C}' p_{\mathrm{C}}' v_{\mathrm{C}}' + d\mathrm{D}' p_{\mathrm{D}}' v_{\mathrm{D}}' + c\int_{\mathrm{C}' p_{\mathrm{C}'}}^{\mathrm{C}'' p_{\mathrm{C}''}} p \cdot \frac{\partial v}{\partial p} \cdot \partial p$$

$$+ d\int_{\mathrm{D}' p_{\mathrm{D}'}}^{\mathrm{D}'' p_{\mathrm{D}''}} p \cdot \frac{\partial v}{\partial p} \cdot \partial p - c\mathrm{C}'' p_{\mathrm{C}}'' v_{\mathrm{C}}'' - d\mathrm{D}'' p_{\mathrm{D}}'' v_{\mathrm{D}}'', \quad \ldots \quad (1)$$

where v_{C}' and v_{C}'' denote the volumes of a molecule C in a partly dissociated state after removal from the reservoirs I. and II. respectively, and v_{D}' and v_{D}'' have similar meanings in respect to a molecule D. These volumes are obtained from the equations

$$v_{\mathrm{C}} = \frac{\mathrm{RT}}{p} + \Sigma \frac{\mathrm{C}_n}{p^n}, \quad \ldots \quad (2)$$

$$v_{\mathrm{D}} = \frac{\mathrm{RT}}{p} + \Sigma \frac{\mathrm{D}_n}{p^n}, \quad \ldots \quad (3)$$

which correspond to the general equation (4) given in the paper quoted. If equation (1) is transformed by means of equations (2) and (3) and the gas equations given in the paper, it assumes the form

$$RT \ln \frac{(p_C'')^c (p_D'')^d}{(p_A'')^a (p_B'')^b} = RT \ln \frac{(p_C')^c (p_D')^d}{(p_A')^a (p_B')^b} + X, \quad . \quad (4)$$

where X is a quantity which vanishes only if the molecules C and D do not dissociate when removed from the reservoirs I. and II. It can then be shown, in exactly the same way as before, that the constant of mass action may be a function of the volume and masses of the interacting constituents as well as of the temperature.

The statement made by Mr. Goldstein that the quantity κ I have introduced is nothing else than the activity coefficient of the concentration term is entirely erroneous, as can best be shown by considering a concrete example. The constant of mass action of a gaseous reaction between the molecules *ce*, c_2, and e_2 in terms of the corresponding molecular activities a_{ce}, a_{c_2}, a_{e_2} is $(a_{ce})^2/a_{c_2}a_{e_2}$, while the expression involving the κ's is $k_1\kappa_1/k_2\kappa_2$, where k_1 expresses the chance of a molecule *ce* encountering another molecule *ce*, and κ_1 the chance of two molecules c_2 and e_2 being formed on account of an encounter, and k_2 and κ_2 have similar meanings. Obviously the κ's are not identical with the a's ; in fact κ is a new and important quantity which is intimately associated with the functional nature of the constant of mass-action, which is a function of the temperature only when the gas equation holds and $\kappa_1 = \kappa_2$.

Yours faithfully,

R. D. Kleeman.

Schenectady, N.Y., U.S.A.

[*The Editors do not hold themselves responsible for the views expressed by their correspondents.*]

Fig. 1.

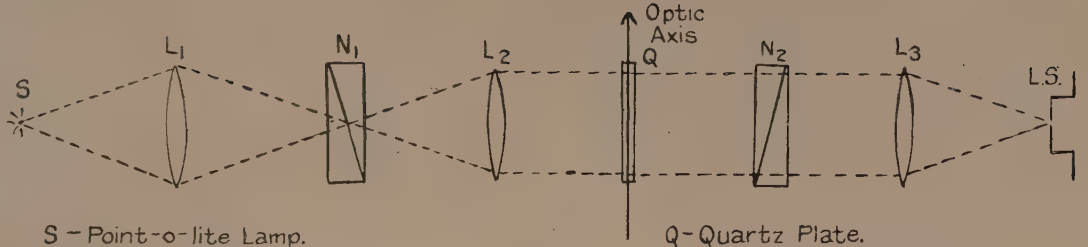
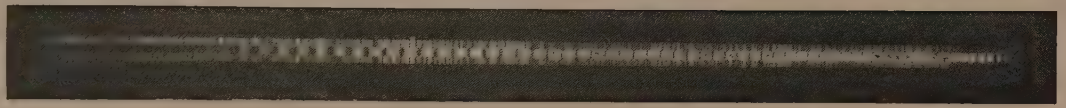
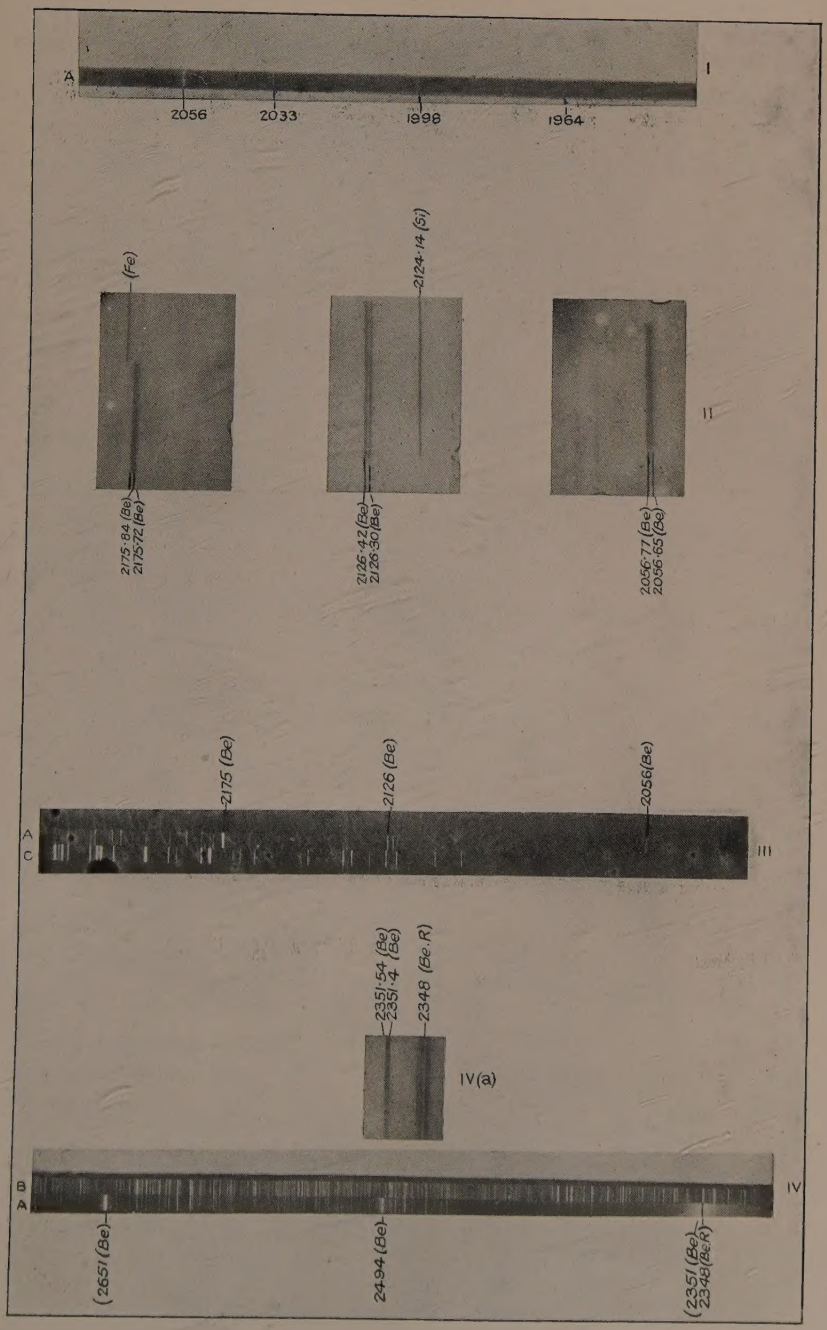
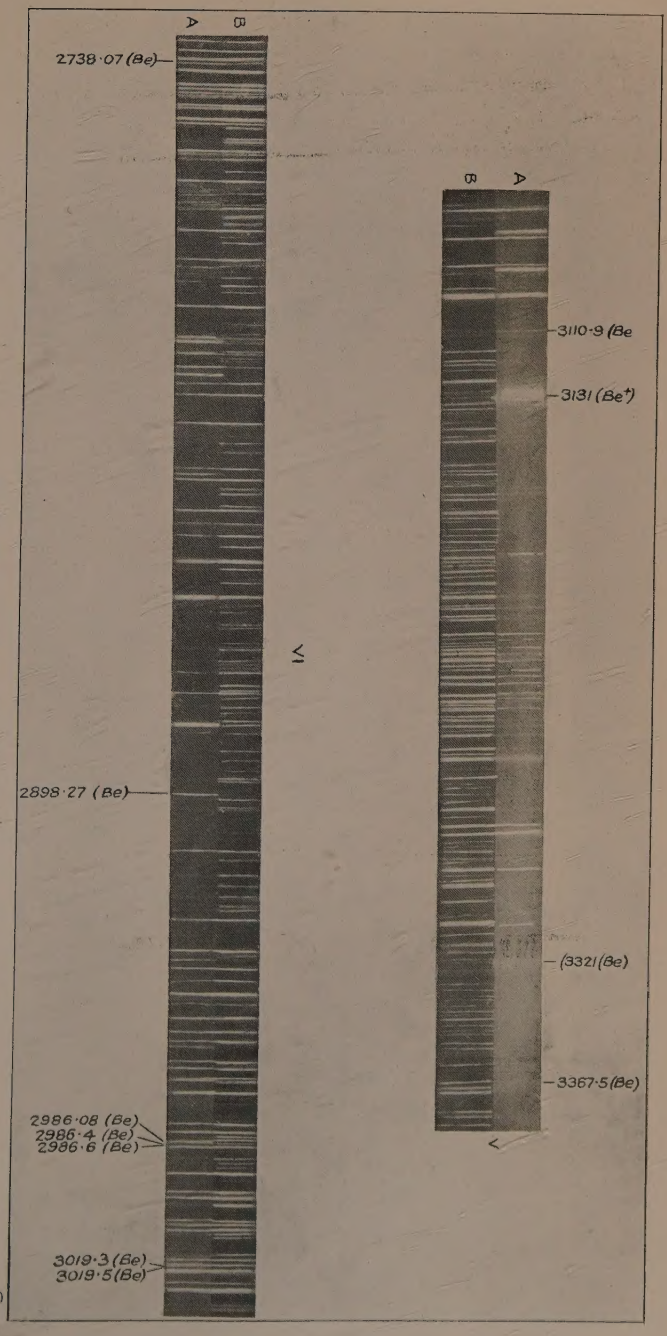

Optic
Axis
S
L1
N1
L2
Q
N2
L3
L.S.
S – Point-o-lite Lamp.
L1L2L3 – Lenses.
N1N2 – Nicols.
Q – Quartz Plate.
L.S. Littrow – Spectrograph.

Fig. 2.





A. Carbon arc fed with Be Salt.
B. Iron arc.
C. Copper arc.



A. Carbon arc fed with Be Salts.
B. Iron Arc.